Studies on The Formation of Trihalomethanes (THMs) and Haloacetic acids (HAAs) during Chlorine and Chlorine dioxide Treatment of Natural Water

By

RANJIB KUMAR PADHI

CHEM02201304005

Indira Gandhi Centre for Atomic Research
Kalpakkam

A thesis submitted to the
Board of Studies in Chemical Sciences
In partial fulfillment of requirements
for the Degree of
DOCTOR OF PHILOSOPHY
of
HOMI BHABHA NATIONAL INSTITUTE

November 2018

Homi Bhabha National Institute

Recommendations of the Viva Voce Committee

As members of the Viva Voce Committee, we certify that we have read the dissertation prepared by **Ranjib Kumar Padhi** entitled "**Studies on The Formation of Trihalomethanes (THMs) and Haloacetic acids (HAAs) during Chlorine and Chlorine dioxide Treatment of Natural Water**" and recommend that it may be accepted as fulfilling the thesis requirement for the award of Degree of Doctor of Philosophy.

Chairman: **Dr. S Rangarajan**
Professor,
Homi Bhabha National Institute
16.07.2019
Signature & Date

Guide / Convener- **Dr. K. K. Satpathy**
Professor (retd.),
Homi Bhabha National Institute
16/7/19
Signature & Date

Examiner: **Dr. M. G. Sujana**
Principal Scientist,
CSIR-IMMT, Bhubaneswar
16/07/19
Signature & Date

Member 1: **Dr. N. Sivaraman**
Professor,
Homi Bhabha National Institute
N. Sivaraman 16.7.19
Signature & Date

Member 2: **T. Subba Rao**
Professor,
Homi Bhabha National Institute
T. S Rao 16/7/2019
Signature & Date

Member 3: **Hrudananda Jena**
Associate Professor,
Homi Bhabha National Institute
16/7/2019
Signature & Date

Final approval and acceptance of this thesis is contingent upon the candidate's submission of the final copies of the thesis to HBNI.

I/We hereby certify that I/we have read this thesis prepared under my/our direction and recommend that it may be accepted as fulfilling the thesis requirement.

Date: 16/07/19
Place: Kalpakkam

Guide: Dr. K. K. Satpathy

STATEMENT BY AUTHOR

This dissertation has been submitted in partial fulfillment of requirements for an advanced degree at Homi Bhabha National Institute (HBNI) and is deposited in the Library to be made available to borrowers under rules of the HBNI.

Brief quotations from this dissertation are allowable without special permission, provided that accurate acknowledgment of source is made. Requests for permission for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the Competent Authority of HBNI when in his or her judgment the proposed use of the material is in the interests of scholarship. In all other instances, however, permission must be obtained from the author.

Ranjib Kumar Padhi

DECLARATION

I, hereby declare that the investigation presented in the thesis has been carried out by me. The work is original and has not been submitted earlier as a whole or in part for a degree/diploma at this or any other Institution / University.

Ranjib Kumar Padhi

List of Publications arising from the thesis

Journal

1. Impact of surface stored groundwater on chlorination and disinfection by-product formation, **R.K. Padhi**, K.K. Satpathy, and S. Subramanian, *Journal of water and health,* **2015,** 13.3, 838-847.

2. Formation, distribution, and speciation of DBPs (THMs, HAAs, ClO_2^-, and ClO_3^-) during treatment of different source water with Chlorine and Chlorine dioxide. **R.K. Padhi**, S Subramanian, K.K Satpathy, *Chemosphere,* **2019,** 218, 540-550

3. Comparative assessment of chlorine reactivity and trihalomethanes formation potential of three different water sources, **R.K. Padhi,** A.K. Mohanty, S Subramanian, K K Satpathy, *Journal of water process Engineering,* **2019,** 29, 100769.

4. Monitoring chlorine residual and trihalomethanes in the chlorinated seawater effluent of the nuclear power plant, **R.K. Padhi,** S. Subramanian, A.K. Mohanty, K.K. Satpathy, Environmental Monitoring and Assessment**, 2019**, In press,doi:10.1007/s10661-019-7611-0

5. Water treatment with Cl_2 and ClO_2: Comparison of two major class of disinfection by-products formation, **R.K. Padhi**, S Subramanian, K.K. Satpathy, *Current Science,* **2018,** Under Review

6. A comparison of the character of algal, bacterial and soil derived organic matter as precursors of disinfection byproducts upon Cl_2 and ClO_2 treatments, R.K. Padhi, S. Subramanian, K. K. Satpathy**, 2018**, Manuscript under preparation

Chapter in book

7. Ecological studies in the coastal waters of Kalpakkam, east coast of India, Bay of Bengal. K.K. Satpathy, A.K. Mohanty, Gouri Sahu, S. Biswas, M.S. Achary, Barath Kumar, R.K. Padhi, N.P.I. Das, S.N. Panigrahi, M.K. Samantara, S.K. Sarkar and R.C. Panigrahy, In: Coastal Management: Global Challenges and Innovations, **2019** (Ed. Krishnamurthy et al.) Elsevier. doi:10.1016/B978-0-12-810473-6.00017-0

Report

8. Environmental Studies with special reference to Aquatic and Terrestrial Systems in and around Kalpakkam, Southeast Coast of India., A.K. Mohanty, R.K. Padhi, Gouri Sahu, M.K. Samantara, N.P.I. Das, S. Panigrahi, Suja Subramanian, M. Sowmya, M.S. Achary, S. Biswas, P. Kumaran, M.K. Velayutham, U. Preethi, K. Navina, G. Sumathi, V.K. Bindu, P. Kolanchiyappan, R. Venkatesan and K.K. Satpathy, IGC Report (IGCAR, Kalpakkam), **2018**, no. 348.

Conferences

1. Chlorination of cooling seawater by NPP: Chlorination by-product formation and discharge, **R.K. Padhi**, S. Subramanian, K.K. Satpathy. Proceedings of the 10th Word Aqua Congress, **2016**, New Delhi, 306-313 pp.

2. Chlorination byproducts formation and discharge due to chlorination of cooling seawater by nuclear power plant, S. Subramanian, **R.K. Padhi**, K.K. Satpathy, Proceedings of the DAE-BRNS theme meeting on chemistry in nuclear technology- CHEMNUT, **2015**, p. 75.

3. Water treatment with chlorine: Influence of source water characteristics on chlorination and CBPs formation. **R.K. Padhi**, S. Subramanian, K.K. Satpathy, Symposium on water chemistry and corrosion in NPPs in Asia, **2015**, Kalpakkam, Chennai, Tamil Nadu, India, p. 64

4. Formation of regulated chlorination byproduct in the cooling seawater discharge of nuclear power plant, K.K. Satpathy, and **R.K. Padhi**, International Congress on Marine Corrosion and Fouling, **2014**, Stephen Riady Centre, National University of Singapore, pp-31.

5. Risk Analysis of trihalomethanes exposure from chlorinated bromide rich drinking water, **R.K. Padhi**, S. Subramanian, M.K. Samantara, M. Sowmya, P. Kumaran, M.V.R. Prasad, and K.K. Satpathy, Int. Conf. on Advancement in materials, Health and Safety towards sustainable energy and Environment, **2014**, Chennai, pp-85.

6. Impact of open storage of subsoil river water on chlorine reactivity and THMs formation, S. Subramanian, **R.K. Padhi**, P. Kumaran and K.K. Satpathy, Int. Conf. on Advancement in materials, Health and Safety towards sustainable energy and Environment, **2014**, Chennai, pp-82.

7. Drinking water disinfection with chlorine: Source water characteristics and formation of toxic chlorination by-products, **R. K. Padhi**, S. Subramanian, K.K. Satpathy, 6th International Congress of Environmental Research, **2013**, Aurangabad.

Ranjib Kumar Padhi

DEDICATION

To my beloved Wife

ROSY

For
Keeping things going smoothly and Always showing how proud she is of me

ACKNOWLEDGEMENTS

Firstly, my sincere thanks and appreciation to my supervisor Dr. K K Satpathy for his guidance, encouragement, and advice in carrying out the Ph.D. work and preparation of the thesis.

I sincerely thank Dr. N. Sivaraman, Dean (Chemical Sciences), IGCAR for his encouraging words every time I met him.

I am grateful to the doctoral committee members, Dr. S. Rangarajan (Chairman), Dr. N. Sivaraman, Dr. T. Subba Rao, and Dr. H. Jena for the evaluation of the work periodically and for their valuable suggestions during the progress of the Ph.D. work.

Special thanks to Ms. S Suja and Ms. G Sumathi for their unconditional cooperation in accomplishing the laboratory experiments in time. I record a special appreciation to both of them for their selfless help and always being there for me throughout the Ph.D. work.

Thanks also to my colleagues Dr. N. P. I. Das, Mr. A. K. Mohanty, Dr. S. N. Panigrahi, Mr. M. K. Samantara and M. Sowmya for their friendly support and help over the years.

Finally, I acknowledge all my family members and friends, for being with me, supported me all the way throughout this work and life in general.

Thank you all

Ranjib Kumar Padhi

CONTENTS

Page no.

SYNOPSIS

Synopsis

Chlorine, a potent oxidizing biocide, has been in use since early 1900s for the disinfection of drinking water [1,2]. Presently, in addition to drinking water treatment, it is also being extensively used in the food industries to ensure microbial safety and in various industrial water utilities for biofouling control. Due to the well-tried technology, long-term worldwide industrial uses, and reasonable cost, chlorination remains the most common treatment in drinking water network and industrial cooling water systems as well. However, chlorine is non-specific and reacts virtually with all the constituents of natural water. Because of these unwanted reactions, a portion of residual chlorine get lost and not available for its biocidal action and the chlorine lost is often referred to as chlorine demand of the water. Wide temporal, as well as spatial variability in the chlorine demand of the natural water, makes it extremely difficult to maintain a precise desired residual in the water circuit and often leads to under chlorination or over-chlorination. Over chlorination causes unnecessary cost to the process as well as adversely affects the environment, whereas, under chlorination leads to the unsuccessful accomplishment of the intended objectives [3]. Thus, chlorine demand of the water needs to be evaluated frequently to maintain an optimum level of chlorination. The advantages of chlorine are overwhelming and have been instrumental in the provision of microbial safe water and fairly successful in combating biofouling.

Notwithstanding the advantages, the drawback associated with chlorine is that, in addition to its intended function, it reacts with natural organic matters (NOMs) present in the natural water to produce a variety of chlorination by-products having a varying degree of persistence and toxicity. In the early 1970s, John Rook, a Dutch chemist, and independently EPA scientists, discovered that water chlorination produces a group of by-products known as trihalomethanes (THMs). Subsequently, other classes of chlorination by-products (CBPs) such as Haloacetic acids (HAAs), Haloacetonitriles (HANs), Haloketones (HKs), Halophenols (HPs) and many more were identified in the chlorinated water [4,5]. Early toxicity tests suggested that these organo-chlorine by-products are toxic even at low parts per billion concentrations. Concern has been expressed since then about the perceived risk to human health due to the CBPs exposure. Several regulatory agencies such as USEPA, WHO has issued strict guidelines [6,7].

The potential of environmental and public health implications sparked the interest in the search for alternatives to chlorine for water disinfection. Efforts were made to find out chlorine alternatives that would avoid these by-products of natural water chlorination. Chemical biocides including ozone, chlorine dioxide, bromine, bromine chloride, and hydrogen peroxide, etc. were examined as potential disinfectants. A few of them such as ClO_2 and O_3 have been used in drinking water disinfection. However, use of most of the chlorine alternative disinfectants in large-scale industrial utilities for biofouling control suffered a setback due to various operational and environmental associated issues. Environmental toxicity, mainly the issue of disinfection by-products remains a concern irrespective the nature of water (freshwater or seawater), although the type and quantity of CBPs may vary in consonance with water quality. The fact that in seawater all of these oxidants yielded the same active ingredient as bromine and thus, similar unwanted, halogenated by-products are expected. Besides, freshwater by-products of these alternatives appeared problematic. For example, the products of ozonation of natural waters could form ozonides, peroxides, and epoxides. Also, new biocides are expected to pose their own set of hazards of unknown environmental and public health concern. Due to the above, the pressure to consider alternatives weakened, and chlorine dominates the water treatment in domestic as well as industrial water utilities.

Apart from chlorine, chlorine dioxide has been used since long as a biocide in many industries such as dairy farm, fruit and vegetable processing, poultry, potable water treatment, and industrial waste treatment. Their use in large-scale water utilities has gained attention recently. ClO_2 has demonstrated promising behavior in a full-scale water distribution system including seawater cooled cooling circuit [8]. Historically, chlorine application to the intake water has been the universal method of choice to combat biofouling in cooling water conduit. The intermittent chlorination practice has always been the most common because slime formation or micro-fouling was observed to be the primary concern. However, where macro-fouling threatened power plant operation (mostly at marine sites), continuous application of chlorine at substantially lower concentrations was found to be effective. As per the earlier studies, the effectiveness of the ClO_2 is at least as high as that of chlorine, even at lower concentration and shorter contact time compared to chlorine. Though numerous inorganic and organic material present in natural water also reacts with ClO_2, many studies have shown that amount of disinfection by-products (DBPs) formed is relatively less as compared to that of chlorine due to the difference in their mechanism of action. Because of their importance in both disinfection of drinking water and control of biofouling in industrial water utilities, the present study is focussed on the use of Cl_2 and ClO_2 for natural water treatment. In water, chlorine dioxide remained as dissolved gas, and properties are substantially different from chlorine. The dominant mechanism of reaction of Cl_2 and ClO_2 with NOMs and other constituents of natural water are different. Type and level of the resultant organic by-products are thus expected to be different. Though the DBPs formed due to ClO_2 treatment of natural water is low compared to chlorine, various factors like pH, temperature, oxidant concentration, NOMs concentration, precursor reactivity may affect the identity and yield of DBPs significantly [9]. Considering the implications, extensive work has been conducted on the various aspects and classes of DBPs formation around the world. However, very few studies that is available from India are restricted only to the assessment of the level of THMs in the chlorinated drinking water. Furthermore, comprehensive studies on the formation of DBPs in real water have been limited to very few water sources worldwide [10].

In addition to the difficulties associated with controlling operational parameters such as temperature, contact time, oxidant dose and environmental conditions; water quality variables, type and amount of natural organic matter (NOMs), and the presence of bromide ion particularly for coastal water contribute further challenges to the accomplishment of effective disinfection. The NOMs in natural water are ill-defined mixture of many chemical constituents that varies temporally and spatially to a great extent. A consequence of this variability is that the specific DBP precursor identification in natural waters is limited. Catchment characteristics of natural water significantly influence both fractional and chemical composition of NOMs. Different types of the natural water source such as seawater, river water, and reservoir water, etc. are expected to have unique NOM signature based on the dominance of autochthonous (Derived from biota from water:

Aquagenic) or allochthonous (from terrestrial input: Pedogenic) origin. Since NOM classification remain uncharacterized to the molecular level [11], there is always uncertainty about the DBPs precursor reactivity in the natural water.

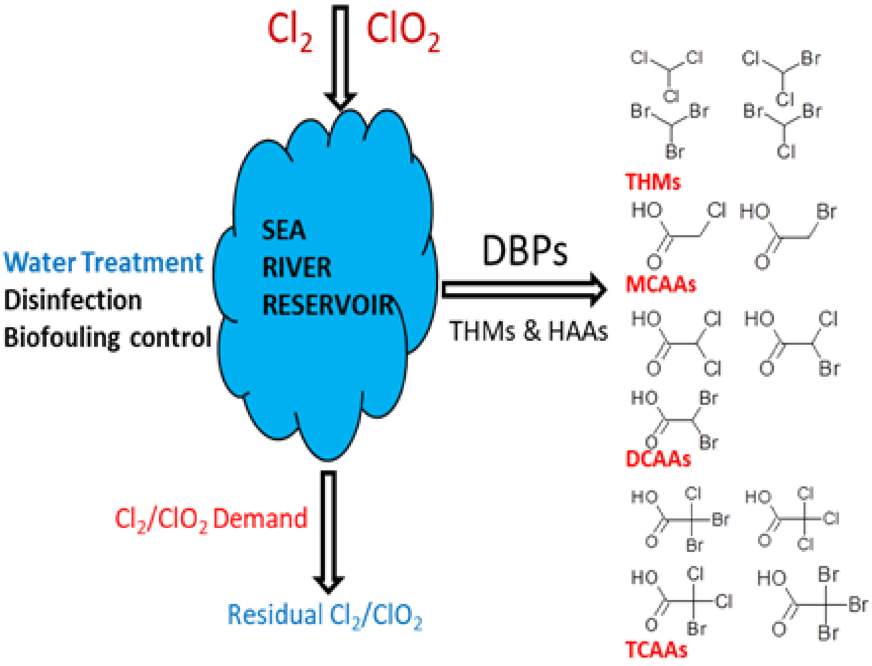


Figure 1. Schematic description of water treatment and DBPs formation

Both effectiveness of disinfection strategy and the identity and yield of DBPs is affected by the disinfectant used, disinfection conditions and water quality descriptors. Understanding the link between physicochemical parameters of the water with DBPs formation and disinfectant efficacy is of prime importance for any natural water system. Moreover, to comprehend the potential impact of changing water treatment option, for example from Cl_2 to ClO_2, it is essential to quantify the formation of different DBPs class for various natural water concurrently. Comparison of data obtained for one class of DBPs in particular natural water with another class of DBPs for a different water source is of no practical use. Similarly, to compare different disinfectants response for DBPs formation, it must be concurrently studied for the water sources. Such information is virtually lacking. Thus, comprehensive input on the comparative behavior of DBPs formed during different treatment options such as Cl_2 and ClO_2 is a prerequisite for the water utility managers to evaluate the potential impact of switching over from one to other.

Keeping the above in the backdrop, the present study was planned to encompass various aspects of water treatment with chlorine and chlorine dioxide for different types of source water. Water samples from three distinct source i.e., seawater, Palar river water, and Open reservoir water collected periodically during the study period. Seawater is being used as condenser cooling water by Madras Atomic Power Station (MAPS) and also will be used for forthcoming nuclear power plants including the Prototype Fast Breeder Reactor (PFBR) at this coast. In addition, it is also used for desalination in the Nuclear Desalination Demonstration Plant (NDDP) located at Kalpakkam industrial complex. Palar river subsoil water and Open reservoir water caters to the domestic and industrial fresh water requirement of various facilities located at Kalpakkam. The open reservoir also caters to the cooling water need for the Fast Breeder Test Reactor (FBTR) present inside the IGCAR complex. The interrelationship of water quality parameters and operational determinants were explored in detail with reference to oxidant reactivity and DBPs formation. Formation of two major class of DBPs, i.e., four THMs and nine HAAs during the oxidant treatment was investigated. Potential NOM precursors in water sources derived from the autochthonous and allochthonous origin for the generation of DBPs was investigated. This thesis contains eight chapters in all. The organization of the thesis is outlined below.

Organization of Thesis

After deliberating briefly on the context, significance, problem, and roadmap of the thesis work in the introduction (Chapter 1), available literature relevant to the present study are closely analyzed and deliberated in Chapter 2. Chapter 3 encompasses the details of material and methodology viz. on the instruments used, sampling procedures, experimental procedures, etc. employed for the thesis work. The core subject of the research works is detailed in the next four chapters. Chapter 4 deals with the studies on the relationship of the physicochemical parameter of source waters with chlorine demand and decay and its inference are extended to discuss the THMs and HAAs formation and discharge in the Madras Atomic Power Station (MAPS) cooling seawater effluent. Detailed investigations on formation kinetics, species distribution of CBPs (THMs and HAAs) during chlorination is provided in Chapter 5. Chapter 6 reports the outcome of the research on the comparative behavior of THMs and HAAs formation during ClO_2 and Cl_2 treatment of water samples from the three distinct sources. The contribution to the NOMs pool of different source water from different allochthonous and autochthonous input and their potential for DBPs formation is discussed in Chapter 7. Finally, the conclusions derived from the present work and the scope for future work constitutes Chapter 8. This dissertation contains seven papers that are in various stages of preparation for publication in peer-reviewed journals. A summary of each Chapter is as follows:

Chapter 1. Introduction

A quick glimpse of the topic in the broader framework of water treatment for disinfection is presented at the beginning. Connections with various aspect of the present study, problem, significance, and scope of the Ph.D. work is stated to contextualize the arrays of information. Use of Chlorination, the discovery of by-products, toxicity concern, regulations, use of ClO_2 as alternative disinfectants, aqueous Cl_2/ClO_2 chemistry, the difficulties, current status, and the information gaps are presented to resonate the research perspective. The content in this chapter also reverberate the importance of two major class of disinfection by-products considered in the present study, i.e. THMs and HAAs and describes the intricacy of natural organic matter precursor in different water sources for CBPs formation.

Chapter 2. Review of literature

Following a brief account of literature on chlorination/chlorine dioxide history and identification of disinfection by-products, appraisal of literatures is narrowed down to the context of present research work. International and national status on the research in the area of the dissertation is underlined. The information on the effect of various parameter affecting the treatment process, particularly chlorine and chlorine dioxide treatment and DBPs formation as reported in the previous studies were analyzed and discussed to draw a reasoned conclusion. Published literature are summarised to exhibit the implications and significance of the present study.

Chapter 3. Materials and Methodology

Chapter-3 systematically describes in details on the study locations, sampling plan, materials, chemicals, and procedures used to conduct the studies. Analytical methodology for extraction, separation, identification, and quantification of four Trihalomethanes and nine haloacetic acids in treated water samples is provided in details. Methods for determination of physicochemical parameters such as dissolved organic matter, bromide, ammonia, residual oxidants, pH, UV absorbance, etc. were mentioned in this section. Laboratory preparation of chlorine dioxide and its standardization is provided. Extraction and XAD-4/XAD-8 fractionation methods of dissolved organic matter from the various origin are illustrated. Analytical conditions for the various instruments used in the thesis work such as gas chromatography-electron capture detector, GC-MS/MS, ion chromatograph-conductivity detector, UV-VIS, TOC Analyser, auto nutrient analyzer, etc. are discussed in details

Chapter 4. Water quality descriptor, chlorine reactivity, and THMs formation

Temporal and spatial variations in the physicochemical characteristics of treated waters significantly influence the effectiveness of the treatment process and formation of DBPs. This chapter contains the results and discussion on the temporal variation of water quality determinants of three water source taken for the study i.e., Seawater, River water, and Reservoir water and their relationship to chlorine decay and THMs formation potential. Residual chlorine and THMs discharge in the Madras Atomic Power Station (MAPS) cooling seawater effluent is also presented in this chapter.

Chapter 5. Formation kinetics and species distribution of THMs during chlorination

Chlorination experiments at different dose have been carried out for three different source water viz. seawater, Palar river water, and reservoir water. Chapter 5 comprises the results on the formation, yield and kinetics of formation of four THMs species in chlorinated water. Effect of bromide on the extent of THMs species shift to Br-THMs for different source water is discussed. Impact of open storage of water on the chlorine decay and THMs formation is described. The interrelationship of dissolved organic content with UVA_{254} and its usefulness as a surrogate to predict THMs formation is discussed. Dependence of dose, temperature and contact time on the species distribution and halogen incorporation is also discussed.

Chapter 6. Comparison of DBPs formation during ClO_2 and Cl_2 treatment

Chapter 6 is dedicated to the studies on the comparative account of THMs and HAAs formation during chlorine and chlorine dioxide treatment of three different natural water sources. Bromine substitution during both the treatment option was interpreted. The contribution of THMs and HAAs to the total CBPs yield was evaluated for chlorine and chlorine dioxide treatment under different conditions. Various aspect of CBPs formation i.e effect of source water on the level of CBPs yield, distribution of THMs and HAAs species, Bromine incorporation during chlorine and chlorine dioxide, etc. are discussed. In addition, results on inorganic DBPs such as Chlorite and Chlorate which is of more concern during ClO_2 treatment is presented.

Chapter 7. THMs and HAAs potential of various NOM sources to water

Chemical characteristics of the dissolved organic matter which also differs considerably among various water sources are supposed to influence the chlorine consumption & the formation of DBPs. Studies are in great need to understand the effect of characteristics of dissolved organic matter derived from different sources on the formation of DBPs. Chapter 7 comprehends the studies on the THMs and HAAs formation potential of various Aquagenic (Algal, Bacterial) and Pedogenic (Soil) organic matter source to natural water on its reaction with chlorine and chlorine dioxide as per the above outline in Figure 6. Extracellular and Intracellular organic matter from three different algae class (blue-green algae, Green Algae & Diatoms), Bacterial mixed culture and water-soluble organic from soil were fractionated. Each of the hydrophilic, hydrophobic and transphilic fractions were tested for chlorine and chlorine dioxide reactivity. THMs and HAAs yield and species distribution were studied for each fraction. Results are analyzed and interpreted extensively in this chapter.

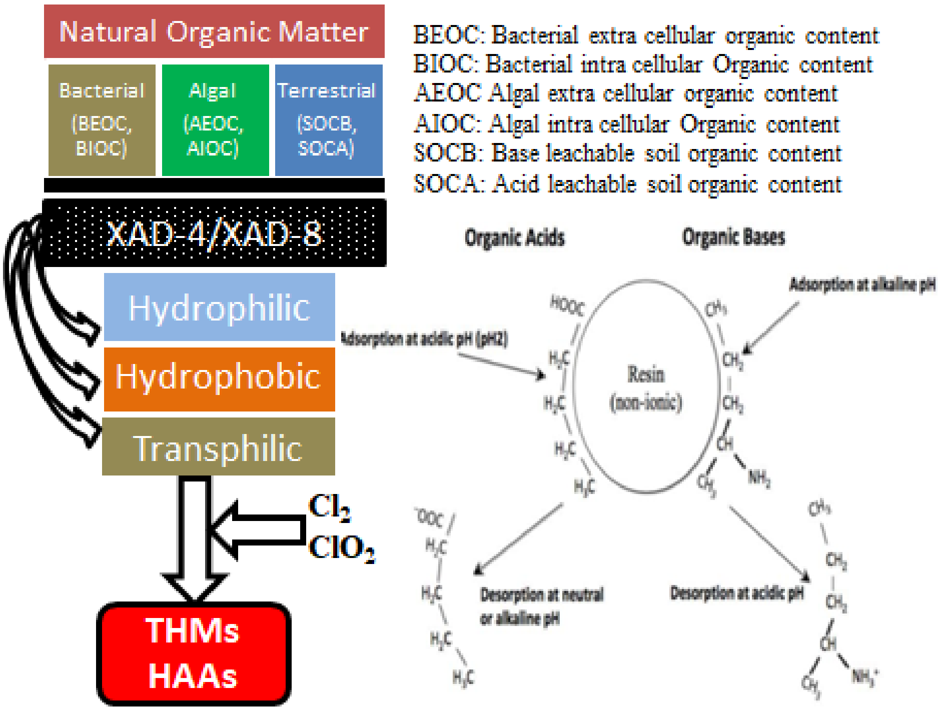


Figure 2. Schematic of the studies on the THMs and HAAs formation potential of various NOM sources (aquagenic & pedogenic) to water

Chapter 8. Summary and Recommendation for future studies

Chapter-8 provides the summary and conclusions of all the studies reported in the thesis and puts forward recommendations for future work. The consequence of lack of correlation between physicochemical properties and DBP formation in a temporal and spatial scale necessitates the identification of more reliable combination determinant for universal DBPs predictions. Recommendation for further research broadly includes characterization of NOM to a deeper level, the fate of CBPs post-formation (post-discharge in case of cooling water effluent), and more studies on real water from different geographical region to reduce data heterogeneity and identification of new by-products formed during disinfection other than chlorination.

References

[1] N.J. Howard, R.E. Thompson, Chlorine Studies and Some Observations on Taste-Producing Substances in Water, and the Factors Involved in Treatment by the Super- and De-Chlorination Methods., J. New Engl. Water Work. Assoc. 40 (1927) 3–276.

[2] H.A. Faber, Super-Chlorination Practice in North America, J. New Engl. Water Work. Assoc. 31 (1939) 9–1539.

[3] Satpathy, K.K., Mohanty, A.K., Sahu, G., Biswas, S., Prasad, M.V.R., Slvanayagam, Biofouling and its control in seawater cooled power plant cooling water system - a review, in: P. Isvetkov (Ed.), Nucl. Power, IntechOpen, Rijeka, 2010: pp. 191–243.

[4] H. Zhai, X. Zhang, Formation and Decomposition of New and Unknown Polar Brominated Disinfection Byproducts during Chlorination, Environ. Sci. Technol. 45 (2011) 2194–2201.

[5] S.E. Hrudey, Chlorination disinfection by-products, public health risk t radeoffs and me, Water Res. 43 (2009) 2057–2092.

[6] S.D. Richardson, M.J. Plewa, E.D. Wagner, R. Schoeny, D.M. Demarini, Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research Antioch-226, (2007).

[7] C. Cortés, R. Marcos, Genotoxicity of disinfection byproducts and disinfected waters: A review of recent literature, Mutat. Res. Toxicol. Environ. Mutagen. 831 (2018) 1–12.

[8] G. Petrucci, M. Rosellini, Chlorine dioxide in seawater for fouling control and post-disinfection in potable waterworks, Desalination. 182 (2005) 283–291.

[9] F. Al-Otoum, M.A. Al-Ghouti, T.A. Ahmed, M. Abu-Dieyeh, M. Ali, Disinfection by-products of chlorine dioxide (chlorite, chlorate, and trihalomethanes): Occurrence in drinking water in Qatar, Chemosphere. 164 (2016) 649–656.

[10] D.M. Golea, A. Upton, P. Jarvis, G. Moore, S. Sutherland, S.A. Parsons, S.J. Judd, THM and HAA formation from NOM in raw and treated surface waters, Water Res. 112 (2017) 226–235.

[11] C. Landry, L. Tremblay, Compositional differences between size classes of dissolved organic matter from freshwater and seawater revealed by an HPLC-FTIR system, Environ. Sci. Technol. 46 (2012) 1700–1707.

List of Figures

Page no.

List of Tables

List of Abbreviations

AEOC: Algal Extracellular Organic Content
AIOC: Algal intracellular Organic Content
AOC: Algal Organic Content
AOM: Algal Organic Matter
BCAA: Bromochloroacetic acid
BDCAA: Bromodichloroacetic Acid
BDCM: Bromodichloromethane
BEOC: Bacterial Extracellular Organic Content
BIOC: Bacterial intracellular Organic Content
BOC: Bacterial Organic Content
Br-THMs: Brominated THM
CBP: Chlorination Byproducts
CD: Chlorine Demand
Chl-a: Chlorophyll-a
CRC: Combined Residual Chlorine
CSW: Condenser Cooling Seawater
CWS: Cooling Water System
DBAA: Dibromoacetic Acid
DBCAA: Dibromochloroacetic Acid
DBCM: Dibromochloromethane
DBP: Disinfection Byproducts
DCAA: Dichloroacetic Acid
DO: Dissolve Oxygen
DOC: Dissolved organic carbon (content)
DOM: dissolved organic Matter
DPD: Di (N, N)-ethyl-p- Phenylene Diamine
ECD: electron Capture detector
FRC: Free Residual Chlorine
HAA: Haloacetic Acid
HAN: Haloacetonitrile
HK: Haloketone
HP: Halophenol
HPI: Hydrophilic
HPO: Hydrophobic
IGCAR: Indira Gandhi Centre for Atomic Research
MAPS: Madras Atomic Power Station
MBAA: Monobromoacetic Acid
MCAA: Monochloroacetic Acid
MP: Mixing Point
MTBE: Methyl Tertiary Butyl Ether
MWe: Megawatt Electricity
NDDP: Nuclear Desalination Demonstration Plant
NOM: Natural Organic Matter
OF: Outfall
OTC: Once-through Cooling
PFBR: Prototype Fast Breeder Reactor
PSW: Process Cooling Seawater
SHAAFP: Specific HAA Formation Potential
SOC: Soil Organic Content

SOCA: Soil Organic Content-Acid Leachable
SOCB: Soil Organic Content-Base (Alkali) Leachable
STHMFP: Specific THM Formation Potential
SUVA: Specific UV absorbance
TBAA: Tribromoacetic Acid
TBM: Tribromomethane
TCAA: Trichloroacetic Acid
TCM: Trichloromethane
THAA: Total HAA
THM: Trihalomethane
TN: Total Nitrogen
TOC: Total Organic carbon
TOX: total organic Halogen
TPI: Transphilic
TRC: Total Residual Chlorine
TRO: Total residual Oxidant
TTHM: Total THM
USEPA: United States Environment Protection Agency
UVA_{254}: UV Absorbance at 254 nm

CHAPTER 1

INTRODUCTION

Chapter 1

Introduction

1.1 Background

Life magazine in 1997, in rating the 100 most important historical events of the previous millennium, declared water chlorination **"*…probably the most significant public health advance of the millennium*,"** ranking it 46th in its list. Chlorine, a potent oxidizing biocide, has been in use since early twentieth century for the disinfection of drinking water [1,2]. Because of its potency, relative ease of use, and lasting residual, chlorine became the most widely adopted and revered disinfectant for water treatment worldwide [3]. Presently, in addition to drinking water treatment, it is also extensively used in many industries, mainly in food industries to ensure microbial safety and for biofouling control in various industrial water utilities like thermal power plants, refineries, petrochemical plants, and chemical processing plants. Due to the well-tried technology, long-term worldwide industrial uses, and reasonable cost, chlorination remains the most common treatment in drinking water network and industrial cooling water systems as well. For the objective of the water chlorination to be served, whether it is drinking water disinfection or biofouling control in industrial water treatment, a desirable level of chlorine residual has to be maintained throughout the water network. However, chlorine is a non-specific oxidant and reacts virtually with all the chemical and biological constituent present in the natural waters. Because of these unwanted reactions, a portion of residual chlorine gets lost and becomes unavailable for its intended biocidal action. The chlorine lost due to these undesired reactions is often referred to as **chlorine demand (CD)** of the water. Physicochemical properties of water such as pH, temperature, chlorophyll, organic matter, ammonia, etc. have an enormous impact on the chlorine demand. Since the water quality parameters show a considerable degree of temporal variations, chlorine demand of water also fluctuates accordingly. Wide temporal, as well as spatial variability in the chlorine demand of the natural water, makes it extremely difficult to maintain a precise desired residual in the water distribution system. The unpredictable variability of chlorine demand often leads to under-chlorination or over-chlorination in the water utilities. Over chlorination causes the unnecessary cost to the process as well as adversely affects the environment, whereas, under-chlorination leads to the unsuccessful accomplishment of the intended objectives [4]. The advantages of chlorine are overwhelming, have been instrumental in the provision of microbial safe water and also fairly successful in combating biofouling. Notwithstanding the advantages, the drawback associated with chlorine is that, in addition to its intended function, it reacts with natural organic matters (NOMs) present in the natural water to produce a variety of chlorination by-products (CBPs) having a varying degree of persistence and toxicity. Evidence published in independent studies by Rooks, (1974) [5] and Bellar et al. (1974) [6] showed that water chlorination produces a group of by-products known as trihalomethanes (THMs). Subsequently, other classes of chlorination by-products (CBPs) such as Haloacetic acids (HAAs), Haloacetonitriles (HANs), Haloketones (HKs), Halophenols (HPs) and many more were identified in the chlorinated water [7,8]. Currently, about many as 700 disinfection by-products (DBPs) have already been identified, and most of them reported to be formed during chlorination of natural water [9–11]. Among these, two major classes of DBPs dominate, and were first to be detected during chlorination of natural water are namely trihalomethanes (THMs), and haloacetic acids (HAAs). THMs consist of four compounds such as chloroform ($CHCl_3$, TCM), bromodichloromethane ($CHBrCl_2$, BDCM), dibromochloromethane ($CHBr_2Cl$, DBCM), and bromoform ($CHBr_3$, TBM) and HAAs consists of nine compounds such as bromoacetic acid ($BrCH_2COOH$, MBAA), chloroacetic acid ($ClCH_2COOH$, MCAA), dibromoacetic acid ($Br_2CHCOOH$, DBAA), dichloroacetic acid ($Cl_2CHCOOH$, DCAA), bromochloroacetic acid (BrClCHCOOH, BCAA), tribromoacetic acid (Br_3CCOOH, TBAA), tri-chloroacetic acid (Cl_3CCOOH, TCAA), dibro-mochloroacetic acid ($Br_2ClCCOOH$, DBCAA), and bromodichloroacetic acid ($BrCl_2CCOOH$, BDCAA). (Note: DBPs refers to the by-products formed during the disinfection of water with various disinfectants such as chlorine, chlorine dioxide, ozone, chloramines, etc., thus include CBPs which generally refers to the by-products identified during chlorination). The discovery of CBPs, because of their proven toxicity, put setback to the untarnished reputation of chlorine as the ‘disinfectant of choice. The attendance and abundance of different DBPs depend on the type of disinfectant used, its dose, and on the array of organic and inorganic constituents present in the source water. The physicochemical features of the raw waters also influence the formation and distribution of various DBPs. Additional variables such as the contact time and the characteristics of the distribution network also play a role in the DBPs formation. When chlorine undergoes substitution reaction with organic matter such as humic acids, fulvic acids, proteins and amino acids present in any natural water; halogenated organics such as THMs and HAAs are formed [12,13]. CBPs formation in water is a function of several factors including temperature, pH, contact time, the concentration of bromides, residual chlorine, and natural DOM [14–16]. Based on the epidemiological investigations, several countries and international organizations such as U.S. Environment Protection Agency (USEPA), World Health Organisation (WHO) have issued strict regulatory guidelines setting the maximum level of THMs and HAAs in finished water [17,18]. Currently, USEPA specifies a maximum contaminant level of 80 µg/L for THMs and 60 µg/L for the sum of five HAAs in the chlorinated finished water [19]. Whereas, WHO has specified guidelines for individual THMs species such as TCM: 300 µg/L, BDCM: 60 µg/L, DBCM: 100 µg/L, TBM: 100 µg/L and HAAs species such as DCAA: 50 µg/L, and TCAA: 20 µg/L [20]. Early toxicity tests have suggested that these chloro-organic by-products are toxic even at low parts per billion concentrations. Even at such low concentrations, these could be carcinogenic, teratogenic and possibly mutagenic [21–25]. Recent studies have linked THMs to cause liver and kidney damage, retarded fetus growth, congenital disabilities, possible miscarriage, congenital disabilities, and possibly miscarriage [24,25]. Some studies showed that HAAs are more carcinogenic than THMs. DCAA was hepatotoxic which promoted the cells accumulating the liver glycogen in rodents [26] and produced neurotoxicity [27]. Both DCAA and DBAA showed adverse male reproductive effects in animal studies [28–30]. Some brominated-HAAs could induce oxidative damages to DNA in the liver [31], found to be toxic for cecal microbiota and reported to be mutagenic [32]. Some investigations have reported that brominated HAAs had minor or more significant adverse health effects than chlorinated-HAAs [31,33,34]. Concerns have been expressed since then about the apparent threat to human health due to the exposure to these carcinogenic CBPs which inextricably forms during the reactions between Cl_2 and NOMs present in the water [24,35].

Historically, apart from drinking water disinfection chlorine application to intake water has been the universal method of choice to combat biofouling in cooling water conduit. Most industrial production processes such as refineries, petrochemical plants, thermal power plant need cooling water for efficient and intermittent operation [36]. Typically, a 500 MW (e) nuclear power plant such as Madras Atomic Power Station (MAPS) at Kalpakkam, Tamil Nadu, India uses about 30 $m^3 s^{-1}$ of cooling water to extract heat from the condenser and other auxiliary heat exchanger systems for its efficient operation [37]. Due to this huge requirement of cooling water, nuclear power plants are preferably being located near the coast to use seawater as cooling water and generally adopts once-through cooling (OTC) water systems. The use of seawater has its disadvantages, biofouling being the major one. Colonization of fouling organisms present in natural water on the various surfaces of the cooling water system (CWS) such as intake structures, screens, pumps, condenser tubes, heat exchangers, etc. greatly hampers smooth operation of the plant and decreases heat transfer efficiency. Unless controlled, biofouling adversely affect the power plant in term of efficiency and structural damage leading to unsafe conditions [38]. Hence, biofouling control has been a prime issue for coastal power plant operation throughout the world. Although various biofouling control methods such as heat treatment, mechanical cleaning, antifouling pains, etc. are available [39], chemical methods have been used traditionally due to the ease of practical applications. Of the several chemical methods available, chlorination is the most commonly used method for biofouling control throughout the word. It is often preferred due to its proven effectiveness, easy availability and relatively low cost [40]. Chlorine has been, in general, applied in two modes such as intermittent and continuous. The intermittent chlorination practice has always been the most common because slime formation or microfouling was observed to be the primary concern. However, where macrofouling threatened power plant operation (mostly at marine sites), continuous application of chlorine at substantially lower concentrations was found to be effective. However, the formation of CBPs during chlorination is a profound concern due to their toxicity [41,42]. In addition to the toxicity concern of these DBPs in drinking water, discharge of the effluent containing these DBPs by the industrial water utilities also lead to the possibility of affecting human health through atmospheric volatilization and subsequent photolysis of brominated compound to reactive oxidants [43,44].

The potential of environmental and public health implications due to the exposure to DBPs triggered the interest in the search for alternatives to chlorine for water disinfection to reduce the possibility of DBPs formation in the disinfected water [45,46]. Efforts were made to find out chlorine alternatives that would avoid these by-products of natural water chlorination. To comply and to reduce the formation and discharge of DBPs, some water utilities considered chemical biocides such as ozone, chloramines, trichlorocyanuric acid, and chlorine dioxide. Chemical biocides including bromine, bromine chloride, hydrogen peroxide, and peracetic acid were also examined as potential disinfectants. A few of them, such as chlorine dioxide (ClO_2) and ozone (O_3) has been used in drinking water disinfection. However, use of most of the chlorine alternative disinfectants in large-scale industrial utilities such as biofouling control in the cooling conduit of thermal power plants impede due to the various operational and associated environmental issues. Environmental toxicity, mainly the issue of DBPs remains a concern irrespective the nature of water (freshwater or seawater), although the type and quantity of CBPs may vary in consonance with water quality. The fact that in seawater all of these oxidants yielded the same active ingredient as bromine and thus, similar unwanted, halogenated by-products are formed. Besides, by-products form in freshwater due to the use of these alternatives also appeared problematic. For example, the products of ozonation of natural waters could form ozonides, peroxides, and epoxides. Moreover, new biocides are expected to pose their own set of hazards of unknown environmental and public health apprehension. Due to the above, the pressure to consider alternatives weakened, and chlorine dominates the water treatment in domestic as well as industrial water utilities.

Among the various Cl_2 alternative, ClO_2 has sustained the popularity in the large-scale water utilities. Chlorine dioxide has been used since long as a biocide in many industries such as dairy farm, fruit and vegetable processing, poultry, potable water treatment, and industrial waste treatment. Their use in large-scale water utilities has gained attention recently. ClO_2 has demonstrated promising behavior in a full-scale water distribution system including seawater cooled cooling circuit [47]. In addition to other advantages, generation of significantly lesser amount of THMs and HAAs as compared to most of the other oxidants has led to its widespread use [48,49]. Though numerous inorganic and organic material present in natural water also reacts with ClO_2, the amount of DBPs formed is relatively less as compared to that of chlorine as it does not undergo substitution reactions with NOMs present in water [50,51]. Many literature reports have evinced, the better effectiveness of chlorine dioxide at lower concentrations than chlorine. In water, chlorine dioxide remained as dissolved gas, and properties are substantially different from chlorine. The dominant mechanism of reaction of Cl_2 and ClO_2 with NOMs and other constituents of natural water are different. Type and level of the resultant organic by-products are thus expected to be different. Though DBPs formed due to ClO_2 treatment of natural water is low compared to chlorine, various factors like pH, temperature, oxidant concentration, NOMs concentration, precursor reactivity may affect the identity and yield of DBPs significantly [52]. In case of water treatment with ClO_2, usually, up to 60% of the applied ClO_2 dose is reduced to chlorite ion, and 8-10% is converted to chlorate ion, and its formation is influenced by the presence of various organic and inorganic constituent in the natural water [51–54]. Further, since the dominant mechanism of reaction of Cl_2 and ClO_2 with NOMs and other constituents of natural water are different, the type and level of the resultant DBPs are expected to be different. Various factors like pH, temperature, oxidant concentration, NOMs concentration, precursor reactivity may affect the formation of DBPs. Besides, the presence of bromide greatly alters the speciation pattern and also known to enhance the concentration of DBPs. In case of water treatment with chlorine dioxide, decomposition of a significant amount of ClO_2 to form inorganic DBPs such as Chlorite (ClO_2^-) and Chlorate (ClO_3^-) are of much concern.

Depending on the availability and use, the requirement of water is fulfilled by various natural water sources such as sea, river and lakes or reservoir. Disinfection of water from freshwater sources such as river and lake reservoir are carried out for providing safe drinking water whereas seawater is disinfected during its use for various purposes such as desalination, aquaculture, cooling water and swimming pool [55–58]. To control the formation of various by-products during oxidant treatment of source water, it is of great importance to know the characteristics of the NOMs precursor for DBPs formation in the source water [59,60]. However, the NOMs in natural water are ill-defined mixture of many chemical constituents that varies temporally and spatially to a great extent. A consequence of this variability is that the specific DBP precursor identification in natural waters is limited. Catchment characteristics of natural water significantly influence both fractional and chemical composition of NOMs. Key factors controlling the formation of DBPs vary from place to place since the source water character is governed by the local geological and hydrological conditions [61]. Water samples from distinct sources, i.e., sea, river, and reservoir contain dissolved organic carbon precursor that have originated from different biochemical processes. Different types of the natural water source such as seawater, river water, and reservoir water, etc. expected to have unique NOM signature based on the dominance of autochthonous (Derived from biota in water: Aquagenic) or allochthonous (from terrestrial input: Pedogenic) origin. Since NOM classification remain uncharacterized to the molecular level [62], there is always uncertainty about the DBPs precursor reactivity in the natural water. In addition to the difficulties associated with controlling operational parameters such as temperature, contact time, oxidant dose and environmental conditions; water quality variables, type and amount of NOMs, and the presence of bromide ion particularly for coastal water contribute further challenges to the accomplishment of effective disinfection. The intricacy of chemical characteristics and features of chlorination in seawater differ greatly from that of fresh waters viz. river water or reservoir water due to the oxidation of bromide present in seawater (~65 mg/L) resulting hypobromous acid (HOBr) as the dominant oxidant species, unlike hypochlorous acid (HOCl) in fresh water. This results into the formation of highly chlorinated DBP like TCM as the dominant fraction during freshwater chlorination whereas, TBM with a very low quantity of DBCM and BDCM dominates in seawater [63–65]. Moreover, bromine-containing biocides are likely to produce more halogenated organics than chlorine [66], but have not been extensively studied.

Considering the above implications, a broad range of studies have been conducted on the various aspects and classes of DBPs formation around the world primarily with respect to drinking water sources and distribution utilities. Scrutiny of available literature shows that information on the formation of DBPs in real water has been limited to very few natural water sources worldwide [67,68]. Moreover, reports related to THM and HAAs production from industrial uses of water, particularly for seawater, are meagrely available. For seawater treatment, a limited number of research available are mainly from seawater desalination followed by nuclear power plant [65,69–71]. Most of the reported investigations have been undertaken for short monitoring duration, and more studies are required for the results to be useful for the management of water works [72]. A very few studies that are available from India are restricted only to the preliminary assessment of the level of THMs in the chlorinated drinking water [73–75]. Both effectiveness of disinfection strategy and the identity and yield of DBPs is affected by the disinfectant used, disinfection conditions and water quality descriptors. Understanding the link between physicochemical parameters of the water with DBPs formation and disinfectant efficacy is of prime importance for any natural water system. Moreover, to comprehend the potential impact of changing water treatment option, for example from Cl_2 to ClO_2, it is essential to quantify the formation of different DBPs class for various natural water concurrently. Comparison of data obtained for one class of DBPs in a particular natural water with another class of DBPs for a different water source is of no practical use. Similarly, to compare different disinfectants response for DBPs formation, it must be concurrently studied for the water sources, for which the information is virtually lacking. Thus, comprehensive input on the comparative behavior of DBPs formed during different treatment options such as Cl_2 and ClO_2 is a prerequisite for the water utility managers to evaluate the potential impact of switching over from one to other.

1.2 Scope and objective of the work

With the above background, this research work was planned to encompass various aspects of oxidant decay and DBPs formation during water treatment with chlorine and chlorine dioxide for three different types of source water i.e, seawater (SWR), Palar river water (RVR) and open reservoir water (RSR) available at Kalpakkam, Tamilnadu, India. Water from these three sources caters to the various need of industrial and domestic use of water at this location. Importantly, 35 $m^3 s^{-1}$ of seawater is used every day for condenser cooling at MAPS which has been subjected to low dose continuous chlorination to maintain a residual of 0.1-0.2 mg/L at the outfall to combat biofouling in the CWS. Seawater will be used as cooling water in forthcoming nuclear power plants including the Prototype Fast Breeder Reactor (PFBR) at this coast. In addition, it is also used for desalination in the Nuclear Desalination Demonstration Plant (NDDP) located at Kalpakkam industrial complex. Palar river subsoil water and Open reservoir water mainly cater to the domestic and industrial fresh water requirement of various facilities located at Kalpakkam. The open reservoir also caters to the cooling water need for the Fast Breeder Test Reactor (FBTR) which is located inside the IGCAR complex. The 10-year-old open reservoir which receives water from the Palar subsoil water endures a massive growth of micro and macro vegetation. The 30,000 m^3 capacity reservoir spreads over an area of about 2 ha with a maximum depth of 3m [76]. Sub-soil water with higher nutrient concentrations when stored in the open air and exposed to the Sunlight results in the growth of planktonic as well as macrophytes plants which can substantially alter the water quality. The resultant increase in the dissolved organic matter (DOM) may affect the water disinfection with respect to both efficacy and DBPs formation. In this connection, the present work comprised of field investigations of Cl_2 residual and THMs discharge at the outfall of MAPS and various laboratory experiment to explore various set objectives as outlined below. The interrelationship of water quality parameters and operational determinants were explored in detail with reference to oxidant reactivity and DBPs formation. Formation of two major class of DBPs, i.e., four THMs and nine HAAs during the oxidant treatment was investigated. Comparative account of DBPs formation with respect to change in different types of source water such as seawater, river water and reservoir was explored. Investigation of the contribution of various aquagenic and pedogenic DBPs precursor during the two oxidants (Cl_2 and ClO_2) treatment scenario was one of the main focuses of the present research. Accordingly, the specific objectives were.

1. Assessment of chlorine reactivity properties in seawater, river water, and reservoir water.
2. Evaluation of THMs discharge at Madras Atomic Power Station (MAPS), Kalpakkam, their temporal behavior and interrelationship with physicochemical parameters

3. Influence of source water quality on the formation behavior of THMs on chlorination.
4. To investigate how open storage of river (Palar river subsoil) water affects the chlorine decay and CBPs formation behavior.
5. To explore the comparative character of formation, distribution and speciation of THMs and HAAs during treatment of different source water with two oxidants namely Cl_2 and ClO_2.
6. To characterize the contribution of various fractions of Aquagenic (Algal, Bacterial) and Pedogenic (Soil) organic matter as THMs and HAAs precursor during Cl_2 and ClO_2 treatment.

References

[1] N.J. Howard, R.E. Thompson, Chlorine Studies and Some Observations on Taste-Producing Substances in Water, and the Factors Involved in Treatment by the Super- and De-Chlorination Methods., J. New Engl. Water Work. Assoc. 40 (1927) 3–276.

[2] H.A. Faber, Super-Chlorination Practice in North America, J. New Engl. Water Work. Assoc. 31 (1939) 9–1539.

[3] H. Galal-Gorchev, Chlorine in Water Disinfection, Pure Appl. Chem. 68 (1996) 1731–1735.

[4] M. Satpathy, K.K., Mohanty, A.K., Sahu, G., Biswas, S., Prasad, M.V.R., Slvanayagam, Biofouling and its control in seawater cooled power plant cooling water system - a review, in: P. Isvetkov (Ed.), Nucl. Power, IntechOpen, Rijeka, 2010: pp. 191–243.

[5] J.J. Rook, Formation of haloforms during chlorination of natural waters, J. Water Treat. Exam. 23 (1974) 234–243.

[6] T.A. Bellar, J.J. Lichtenberg, R.C. Kroner, The Occurrence of Organohalides in Chlorinated Drinking Waters, J. Am. Water Works Assoc. 66 (1974) 703–706.

[7] H. Zhai, X. Zhang, Formation and Decomposition of New and Unknown Polar Brominated Disinfection Byproducts during Chlorination, Environ. Sci. Technol. 45 (2011) 2194–2201.

[8] S.E. Hrudey, Chlorination disinfection by-products, public health risk tradeoffs and me, Water Res. 43 (2009) 2057–2092.

[9] D. Liviac, E.D. Wagner, W.A. Mitch, M.J. Altonji, M.J. Plewa, Genotoxicity of Water Concentrates from Recreational Pools after Various Disinfection Methods, Environ. Sci. Technol. 44 (2010) 3527–3532.

[10] M. Yang, X. Zhang, Current trends in the analysis and identification of emerging disinfection byproducts, Trends Environ. Anal. Chem. 10 (2016) 24–34.

[11] J. Han, X. Zhang, Evaluating the Comparative Toxicity of DBP Mixtures from Different Disinfection Scenarios: A New Approach by Combining Freeze-Drying or Rotoevaporation with a Marine Polychaete Bioassay, Environ. Sci. Technol. 52 (2018) 10552–10561.

[12] S. Fam, M.K. Stenstrom, Precursors of Non-Volatile Chlorination By-Products, J. (Water Pollut. Control Fed. 59 (1987) 969–978.

[13] S.K. Gang, D. C., Clevenger, T. E., & Banerji, Modeling Chlorine Decay in Surface Water, J. Environ. Informatics. 1 (2003) 21–27.

[14] S.K. Golfinopoulos, G.B. Arhonditsis, Multiple regression models: A methodology for evaluating trihalomethane concentrations in drinking water from raw water characteristics, Chemosphere. 47 (2002) 1007–1018.

[15] A.D. Nikolaou, S.K. Golfinopoulos, T.D. Lekkas, M.N. Kostopoulou, DBP levels in chlorinated drinking water: Effect of humic substances, Environ. Monit. Assess. 93 (2004) 301–319.

[16] B. Ye, W. Wang, L. Yang, J. Wei, Factors influencing disinfection by-products formation in drinking water of six cities in China, J. Hazard. Mater. 171 (2009) 147–152.

[17] S.D. Richardson, M.J. Plewa, E.D. Wagner, R. Schoeny, D.M. Demarini, Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research Antioch-226, (2007).

[18] C. Cortés, R. Marcos, Genotoxicity of disinfection byproducts and disinfected waters: A review of recent literature, Mutat. Res. Toxicol. Environ. Mutagen. 831 (2018) 1–12.

[19] USEPA, National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfection Byproducts Rule; Final rule, (2006) 399–493.
[20] WHO, WHO guidelines for drinking-water quality-4th edition, 2011.
[21] S. Lee, H. Guo, S.M. Lam, S.L. Lau, Multipathway risk assessment on disinfection by-products of drinking water in Hong Kong, Environ. Res. 94 (2004) 47–56.
[22] R.S. Zhao, X.T. Wang, A.X. Wei, X.B. Xu, Determination of Trihalomethanes in Drinking Water from Beijing , People ' s Republic of China, Bull. Environ. Contam. Toxicol. 73 (2004) 111–116.
[23] M.A. Stack, G. Fitzgerald, S. O'Connell, K.J. James, Measurement of trihalomethanes in potable and recreational waters using solid phase micro extraction with gas chromatography-mass spectrometry., Chemosphere. 41 (2000) 1821–6.
[24] D. Ristoiu, U. von Gunten, A. Mocan, R. Chira, B. Siegfried, M. Haydee Kovacs, S. Vancea, Trihalomethane formation during water disinfection in four water supplies in the Somes river basin in Romania., Environ. Sci. Pollut. Res. Int. 16 Suppl 1 (2009) S55–S65.
[25] J.M. Wright, J. Schwartz, D.W. Dockery, The effect of disinfection by-products and mutagenic activity on birth weight and gestational duration., Environ. Health Perspect. 112 (2004) 920–5.
[26] J. Kato-Weinstein, M.K. Lingohr, G.A. Orner, B.D. Thrall, R.J. Bull, Effects of dichloroacetate on glycogen metabolism in B6C3F1 mice, Toxicology. 130 (1998) 141–154.
[27] P.W. Stacpoole, The pharmacology of dichloroacetate., Metabolism. 38 (1989) 1124–44.
[28] J.L. Cicmanec, L.W. Condie, G.R. Olson, S.-R. Wang, 90-Day toxicity study of dichloroacetate in dogs, Fundam. Appl. Toxicol. 17 (1991) 376–389.
[29] G.P. Toth, K.C. Kelty, E.L. George, E.J. Read, M.K. Smith, Adverse male reproductive effects following subchronic exposure of rats to sodium dichloroacetate., Fundam. Appl. Toxicol. 19 (1992) 57–63.
[30] R.E. Linder, G.R. Klinefelter, L.F. Strader, J.D. Suarez, C.J. Dyers, Acute Spermatogenic Effects of Bromoacetic Acids, Fundam. Appl. Toxicol. 22 (1994) 422–430.
[31] J.M. Parrish, E.W. Austin, D.K. Stevens, D.H. Kinder, R.J. Bull, Haloacetate-induced oxidative damage to DNA in the liver of male B6C3F1 mice., Toxicology. 110 (1996) 103–11.
[32] G.M. Nelson, A.E. Swank, L.R. Brooks, K.C. Bailey, S.E. George, Metabolism, microflora effects, and genotoxicity in haloacetic acid-treated cultures of rat cecal microbiota., Toxicol. Sci. 60 (2001) 232–41.
[33] E.W. Austin, J.M. Parrish, D.H. Kinder, R.J. Bull, Lipid peroxidation and formation of 8-hydroxydeoxyguanosine from acute doses of halogenated acetic acids., Fundam. Appl. Toxicol. 31 (1996) 77–82.
[34] S. Giller, F. Le Curieux, F. Erb, D. Marzin, Comparative genotoxicity of halogenated acetic acids found in drinking water., Mutagenesis. 12 (1997) 321–8.
[35] H. Gallard, U. Von Gunten, Chlorination of natural organic matter: Kinetics of chlorination and of THM formation, Water Res. 36 (2002) 65–74.
[36] M. Al-Bloushi, J. Saththasivam, S. Jeong, G.L. Amy, T.O. Leiknes, Effect of organic on chemical oxidation for biofouling control in pilot-scale seawater cooling towers, J. Water Process Eng. 20 (2017) 1–7.
[37] K.K. Satpathy, A.K. Mohanty, G. Sahu, S.K. Sarkar, U. Natesan, R. Venkatesan, M.V.R. Prasad, Variations of physicochemical properties in Kalpakkam coastal waters, east coast of India, during southwest to northeast monsoon transition period, Environ. Monit. Assess. 171 (2010) 411–424.
[38] K.V.K. Nair, Marine biofouling and its control with particular reference to condenser-cooling circuits of power plants - an overview, J. Indian Inst. Sci. 79 (1999) 497–511.

[39] F.T. J. W. Whitehouse, J. Coughlan, B. G. Lewis, The Control of Biofouling in Marine and Estuarine Power Stations, Cent. Electr. Gener. Board. (1985) 48.

[40] K.K. Satpathy, Studies on the chemical features of cooling water systems in the context of scaling, biofouling and corrosion control, Madras University, India, 1996.

[41] M.J. Plewa, Y. Kargalioglu, D. Vankerk, R.A. Minear, E.D. Wagner, Mammalian cell cytotoxicity and genotoxicity analysis of drinking water disinfection by-products, Environ. Mol. Mutagen. 40 (2002) 134–142.

[42] Y. Pan, X. Zhang, Y. Li, Identification, toxicity and control of iodinated disinfection byproducts in cooking with simulated chlor(am)inated tap water and iodized table salt, Water Res. 88 (2016) 60–68.

[43] J. Deng, C. Liu, L. Yu, B. Zhou, Chronic exposure to environmental levels of tribromophenol impairs zebrafish reproduction, Toxicol. Appl. Pharmacol. 243 (2009) 87–95.

[44] J. Parinet, S. Tabaries, B. Coulomb, L. Vassalo, J.-L. Boudenne, Exposure levels to brominated compounds in seawater swimming pools treated with chlorine, Water Res. 46 (2012) 828–836.

[45] S.W. Krasner, M.J. McGuire, J.G. Jacangelo, N.L. Patania, K.M. Reagan, E.M. Aieta, The Occurrence of Disinfection By-products in US Drinking Water, J. Am. Water Works Assoc. 81 (1989) 41–53.

[46] H. Arora, M.W. LeChevallier, K.L. Dixon, DBP occurrence survey, J. Am. Water Works Assoc. 89 (1997) 60–68.

[47] G. Petrucci, M. Rosellini, Chlorine dioxide in seawater for fouling control and post-disinfection in potable waterworks, Desalination. 182 (2005) 283–291.

[48] W. Gan, H. Huang, X. Yang, Z. Peng, G. Chen, Emerging investigators series: disinfection by-products in mixed chlorine dioxide and chlorine water treatment, Environ. Sci. Water Res. Technol. 2 (2016) 838–847.

[49] G. Gordon, B. Slootmaekers, S. Tachiyashiki, W.W.I. Delmer, Minimizing Chlorite Ion and Chlorate Ion in Water Treated With Chlorine Dioxide, J. Am. Water Works Assoc. 82 (1990) 160–165.

[50] C. Korn, R.C. Andrews, M.D. Escobar, Development of chlorine dioxide-related by-product models for drinking water treatment, Water Res. 36 (2002) 330–342.

[51] X. Yang, W. Guo, W. Lee, Formation of disinfection byproducts upon chlorine dioxide preoxidation followed by chlorination or chloramination of natural organic matter, Chemosphere. 91 (2013) 1477–1485.

[52] F. Al-Otoum, M.A. Al-Ghouti, T.A. Ahmed, M. Abu-Dieyeh, M. Ali, Disinfection by-products of chlorine dioxide (chlorite, chlorate, and trihalomethanes): Occurrence in drinking water in Qatar, Chemosphere. 164 (2016) 649–656.

[53] J. Han, X. Zhang, J. Liu, X. Zhu, T. Gong, Characterization of halogenated DBPs and identification of new DBPs trihalomethanols in chlorine dioxide treated drinking water with multiple extractions, J. Environ. Sci. 58 (2017) 83–92.

[54] S. Sorlini, F. Gialdini, M. Biasibetti, C. Collivignarelli, Influence of drinking water treatments on chlorine dioxide consumption and chlorite/chlorate formation, Water Res. 54 (2014) 44–52.

[55] S. Chowdhury, K. Alhooshani, T. Karanfil, Disinfection byproducts in swimming pool: Occurrences, implications and future needs, Water Res. 53 (2014) 68–109.

[56] T. Manasfi, M. De Méo, B. Coulomb, C. Di Giorgio, J.-L. Boudenne, Identification of disinfection by-products in freshwater and seawater swimming pools and evaluation of genotoxicity, Environ. Int. 88 (2016) 94–102.

[57] J. Wang, Z. Hao, F. Shi, Y. Yin, D. Cao, Z. Yao, J. Liu, Characterization of Brominated Disinfection Byproducts Formed During the Chlorination of Aquaculture Seawater, Environ. Sci. Technol. 52 (2018) 5662–5670.

[58] R. Xue, H. Shi, Y. Ma, J. Yang, B. Hua, E.C. Inniss, C.D. Adams, T. Eichholz, Evaluation of thirteen haloacetic acids and ten trihalomethanes formation by peracetic acid and chlorine drinking water disinfection, Chemosphere. 189 (2017) 349–356.

[59] R.K. Padhi, K.K. Satpathy, S. Subramanian, Impact of groundwater surface storage on chlorination and disinfection by-product formation, J. Water Health. 13 (2015) 838.

[60] Z. Yang, Y.-X. Sun, T. Ye, N. Shi, F. Tang, H.-Y. Hu, Characterization of trihalomethane, haloacetic acid, and haloacetonitrile precursors in a seawater reverse osmosis system, Sci. Total Environ. 576 (2017) 391–397.

[61] H. Hong, Y. Xiong, M. Ruan, F. Liao, H. Lin, Y. Liang, Factors affecting THMs, HAAs and HNMs formation of Jin Lan Reservoir water exposed to chlorine and monochloramine, Sci. Total Environ. 444 (2013) 196–204.

[62] C. Landry, L. Tremblay, Compositional differences between size classes of dissolved organic matter from freshwater and seawater revealed by an HPLC-FTIR system, Environ. Sci. Technol. 46 (2012) 1700–1707.

[63] R.K. Padhi, M. Sowmya, A.K. Mohanty, S.N. Bramha, K.K. Satpathy, Formation and speciation characteristics of brominated trihalomethanes in seawater chlorination, Water Environ. Res. 84 (2012) 2003–2009.

[64] M. Fabbricino, G. V. Korshin, Formation of disinfection by-products and applicability of differential absorbance spectroscopy to monitor halogenation in chlorinated coastal and deep ocean seawater, Desalination. 176 (2005) 57–69.

[65] H.A. Jenner, C.J.L. Taylor, M. Van Donk, M. Khalanski, Chlorination by-products in chlorinated cooling water of some European coastal power stations, Mar. Environ. Res. 43 (1997) 279–293.

[66] E. Agus, N. Voutchkov, D.L. Sedlak, Disinfection by-products and their potential impact on the quality of water produced by desalination systems: A literature review, Desalination. 237 (2009) 214–237.

[67] D.M. Golea, A. Upton, P. Jarvis, G. Moore, S. Sutherland, S.A. Parsons, S.J. Judd, THM and HAA formation from NOM in raw and treated surface waters, Water Res. 112 (2017) 226–235.

[68] M.P. Abdullah, L.F. Yee, S. Ata, A. Abdullah, B. Ishak, K.N.Z. Abidin, The study of interrelationship between raw water quality parameters, chlorine demand and the formation of disinfection by-products, Phys. Chem. Earth. 34 (2009) 806–811.

[69] C.J.L.L. Taylor, The effects of biological fouling control at coastal and estuarine power stations, Mar. Pollut. Bull. 53 (2006) 30–48.

[70] E. Agus, D.L. Sedlak, Formation and fate of chlorination by-products in reverse osmosis desalination systems, Water Res. 44 (2010) 1616–1626.

[71] M. Khalanski, H.A. Jenner, Chlorination chemistry and ecotoxicology of the marine cooling water systems, in: Oper. Environ. Consequences Large Ind. Cool. Water Syst., Springer US, Boston, MA, 2012: pp. 183–226.

[72] B. Ramavandi, S. Farjadfard, M. Ardjmand, S. Dobaradaran, Effect of water quality and operational parameters on trihalomethanes formation potential in Dez River water, Iran, Water Resour. Ind. 11 (2015) 1–12.

[73] M. Satyanarayana, M., Chandrasekhar, Occurence and control of trihalomethanes in drinking water supplies, Indian J. Environ. Prot. 16 (1996) 423–426.

[74] N.P. Thacker, V. Nitnaware, Factors influencing formation of trihalomethanes in swimming pool water, Bull. Environ. Contam. Toxicol. 71 (2003) 633–640.

[75] N.P. Thacker, P. Kaur, A. Rudra, Trihalomethane Formation Potential and Concentration Changes During Water Treatment at Mumbai (India), Environ. Monit. Assess. 73 (2002) 253–262.

[76] K.K. Satpathy, K.V.K. Nair, P.K. Mathur, Chlorine demand & chemical control of biofouling in power plant cooling system, in: M.P. Thompson, R. Nagabhushanam (Eds.), Recent Dev. Biofouling Control, Oxford Oxford & IBH Publishing Company, New Delhi, 1994: pp. 397–407.

CHAPTER 2

LITERATURE REVIEW

Chapter 2

Literature review

2.1 History of Chlorination

Chlorine is by far the most commonly used chemical for disinfection of water supplies. It is also active for other purposes associated with water treatment and supply, such as prevention of algal, bacterial and general slime growths in treatment plants and pipe-works, control of tastes and odors, and removal of iron, manganese, and color [1]. Chlorine was discovered in 1774 by **Karl W Scheele** and identified as an element in 1810 by **Humphrey Davy**. One of the first reported uses of chlorine for the disinfection of water supplies was in 1897 when bleach solution was used to disinfect water main in Maidstone, Kent, UK, following an outbreak of typhoid. Regular use in water treatment began around the beginning of the twentieth century. Probably, the first continuous application was in 1902 at Middelkerke, Belgium. In 1908 in Chicago, IL, USA. The technique for the purification of drinking water by use of compressed liquefied chlorine gas was developed by a British officer **Vincent B. Nesfield**, in the Indian Medical Service, in 1903. **Major Carl Rogers Darnall**, Professor of Chemistry at the Army Medical School, gave the first practical demonstration of this in 1910. This work became the basis for present day systems of municipal water purification. Shortly after Darnall's demonstration, **Major William J. L. Lyster** of the Army Medical Department used a solution of calcium hypochlorite in a linen bag to treat water. In 1910-20, technology to store and transport liquid chlorine was developed, and the design of suitable chlorinator installations led to increased use of chlorine, providing easier control, monitoring and better disinfection than the various hypochlorite solutions. Notable in these and subsequent developments in the field of water treatment with chlorine were **Wallace and Tiernan**, who patented a variety of control and safety devices [1]. The introduction of chlorine-resistant plastics in the 1950s and increased understanding of the chemistry of chlorination accelerated the process. Further major developments were the use of ammonia-chlorine reactions and the breakpoint phenomenon to minimize the taste and odor of chlorine, precise control of chlorine residues by de-chlorination with sulfur dioxide and, more recently, concern over organic chemical by-products and the possible need for their control. Since that time the endorsement and prevalent applications of free residual chlorine evolved as a result of developments in our knowledge of chlorine chemistry and the biocidal capabilities of various forms of chlorine [2,3]. Since the early 1970s, the presences of disinfection by-products (DBPs) formed by reaction of chlorine with other compounds in the water was noted, and possible health effects of DBPs were investigated. This led to the first DBP rule in 1979, and U.S. EPA set an interim maximum contaminant level of 100 µg/L for trihalomethanes. As additional knowledge about DBPs was gained, a Stage 1 Disinfectants and Disinfection Byproducts Rule was issued in 1998, and the currently effective Stage 2 Rule was issued in 2006 which specifies a maximum contaminant level of 80 µg/L for THMs and 60 µg/L for the sum of five HAAs. As a strong oxidizing agent, chlorine kills via the oxidation of organic molecules. Chlorine and its hydrolysis product hypochlorous acid are neutrally charged and therefore easily penetrate the negatively charged surface of pathogens. It can disintegrate the lipids that compose the cell wall and react with intracellular enzymes and proteins, making them non-functional. Microorganisms then either die or are no longer able to multiply. In addition to chlorine, chlorine dioxide has emerged to be an alternative to chlorine because it is an oxidizing agent rather than a chlorinating agent, and therefore, not expected to form chlorinated disinfection by-products such as HAAs and THMs under typical water treatment conditions. Chlorine dioxide, discovered in 1811 by Sir Humphrey Davy, who called the green-yellow gas as chlorine and first reported use was in 1944 in water treatment at New York [4]. Use of chlorine dioxide has now expanded to numerous industries including wood pulp processes, wastewater treatment, and food processing, etc.

2.2 Aqueous Chemistry of Chlorine

Chlorine for water treatment is usually applied either in the form of compressed gas or as solutions of hypochlorite (sodium hypochlorite (NaOCl) or solid calcium hypochlorite (Ca $(OCl)_2$), and it hydrolyzes in water as per the following eqs 2.1-2.4 [5]

$$\mathrm{Cl_2 + H_2O \leftrightarrow HOCl + H^+} \quad (2.1)$$

$$\mathrm{NaOCl + H_2O \rightarrow HOCl + Na^+ + OH^-} \quad (2.2)$$

$$\mathrm{Ca(OCl)_2 + H_2O \rightarrow 2HOCl + Ca^+ + 2OH^-} \quad (2.3)$$

$$\mathrm{HOCl \leftrightarrow OCl^- + H^+} \quad (2.4)$$

The total concentration of molecular chlorine (Cl_2), hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) are defined as ‘free available chlorine.’ In water containing ammonia and other nitrogen compounds, Cl_2 reacts with them to produce chloramines (NH_2Cl, $NHCl_2$, and NCl_3 as per equations 2.5-2.7) and organic chloramines which are referred to as “combined chlorine.” Total chlorine measured is the sum of both free and combined chlorine. Combined chlorine has a disinfection property with less efficiency than that of free chlorine [1,5]. The unusual phenomenon during chlorination of water containing ammonia, results in an initial increase in combined chlorine residual, followed by a decrease in the combined chlorine residual along with ammonia concentration, followed by an increase in free chlorine residual and near complete removal of ammonia as nitrogen gas was first explained by Griffin, (1939) [6] and used the term breakpoint to describe the point where chlorine and ammonia concentrations were simultaneously minimized (**Figure 2.1**).

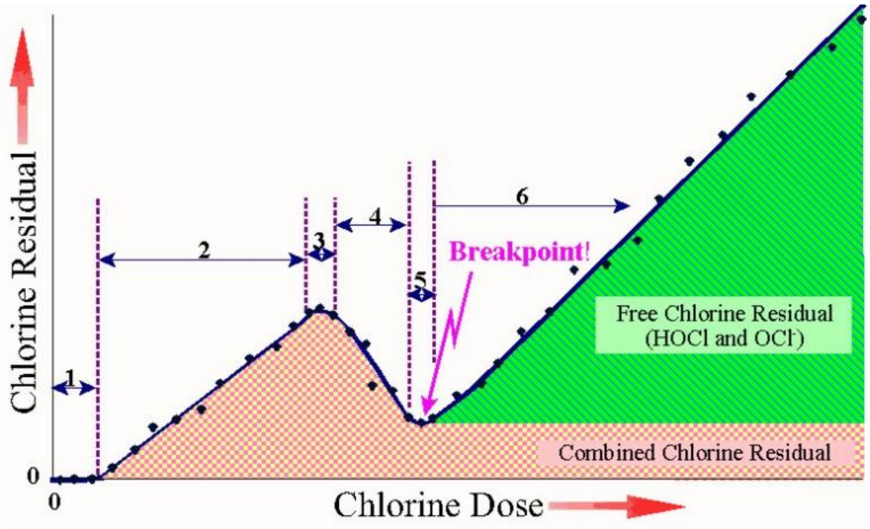


Figure 2. 1 Representation of breakpoint chlorination with different zones of dominant reactions; 1: Chlorine reactions with rapidly oxidisable substances such as Fe+2, Mn+2, and S-2; 2: reactions with ammonia and organic nitrogen compounds to produce chloramines (dominantly monochloramines); 3: transition zone; 4: Conversion of monochloramine to dichloramines followed by trichloramines and their destruction making the slope negative; 5: Break-point where all nitrogen gets oxidised and residual chlorine begins to persists; 6: Available of free residual chlorine proportional to applied chlorine dose with minor presence of monochloramine, trichloramine and organochloramines

Later, extensive contribution to the kinetics of breakpoint chlorination and stoichiometry of reactions were made by many authors [7–10]. Generally, in the presence of excess ammonia to chlorine molar concentration, monochloramine is the main product. However, dichloramine, followed by trichloramine are produced dominantly when molar chlorine concentrations exceed that of ammonia [11,12].

$$\mathrm{NH_3 + HOCl \rightarrow NH_2Cl + H_2O} \qquad (2.5)$$

$$\mathrm{NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O} \qquad (2.6)$$

$$\mathrm{NHCl_2 + HOCl \rightarrow NCl_3 + H_2O} \qquad (2.7)$$

Figure 2. 1 represents the oversimplified illustration of breakpoint chlorination. Chloramines as mentioned earlier also have the biocidal capacity lesser than chlorine [13], also commonly used for water treatment. However, Turetgen (2004) [14] observed monochloramine to be significantly more effective than chlorine against biofilm removal. The biocidal capacity of chloramines follows the order $NHCl_2$ > NH_2Cl > NCl_3, and their concentration ratio mainly depends on the ammonia concentration and pH of the raw water [15]. Apart from ammonia organic nitrogenous material such as amino acids and proteins are sources of organic chloramine formation during chlorination. Organic chloramines are weaker disinfectant than inorganic chloramines [16]. Chlorine is a non-selective oxidant, virtually reacts with almost all constituents present in the water. The reaction with the most reactive inorganic substance in their reduced valence states such as ammonia, sulfide, cyanide, nitrite, iron, and manganese are usually fast reactions occurring within seconds to minutes [17–20]. The reactions with organic matter in water usually occur at a relatively slower rate. Both the organic and inorganic matter present in the water at varying concentrations and having a different degree of reactivity cause a gradual loss of chlorine in a treatment process. These reactions result into partial loss of chlorine to be available for intended function and often referred to as **Chlorine Demand**. There is a great deal of interest in understanding the factors that affect the chlorine demand and the dose of chlorine during chlorination [17,21–24]. A number of parameters, more importantly, type and concentration of inorganic and organic content, temperature,

pH, and initial chlorine concentration affect the chlorine demand [17]. During water chlorination, depending on the pH of the water, Cl_2, HOCl, and OCl^- exists in equilibrium with each other (Dore´, 1989). At the typical pH that exists for natural water, the equilibrium between HOCl and OCl^- (eq. 2.4) is the most important. Temperature and chloride concentration also affect the distribution to some extent [19]. Apart from these major chlorine species, trichloride (Cl_3^-), chlorine hemioxide (Cl_2O) were also reported [25,26], which generally present at a very low concentration under typical water treatment conditions [27,28]. Under the usually observed pH range of 6-9 during water treatment, HOCl and OCl^- are the main reactive species. Among these, HOCl, being neutral can penetrate the negative surface of pathogens more readily than negative OCl^- ion and thus is more powerful as a disinfectant than OCl^- [29]. In natural water, bromide is ubiquitously present at varying concentration with higher concentrations generally observed for water sources located at coastal sites with a highest of ~65 mg/L is present in seawater. Presence of bromide complicates the water treatment with chlorination. During chlorination of water containing bromide, due to the chlorine and bromide standard redox potentials, bromide gets rapidly oxidized to HOBr which exists with OBr^- (eq. 2.8) in pH-dependent equilibrium like HOCl and OCl^- in water.

$$\mathrm{HOCl} + \mathrm{Br}^- \leftrightarrow \mathrm{HOBr} + \mathrm{Cl}^- \qquad (2.8)$$

At pH of about 8.0, OCl^- dominates (80%) for HOCl ↔ OCl^- equilibrium, whereas HOBr is the main fraction (80%) for HOBr ↔ OBr- equilibrium (**Figure 2. 2**). Thus, during seawater chlorination, HOBr is the dominant reactive oxidant species. Since HOBr and HOCl are stronger disinfectants than their corresponding anions, it offers a great advantage during seawater chlorination as discussed later.

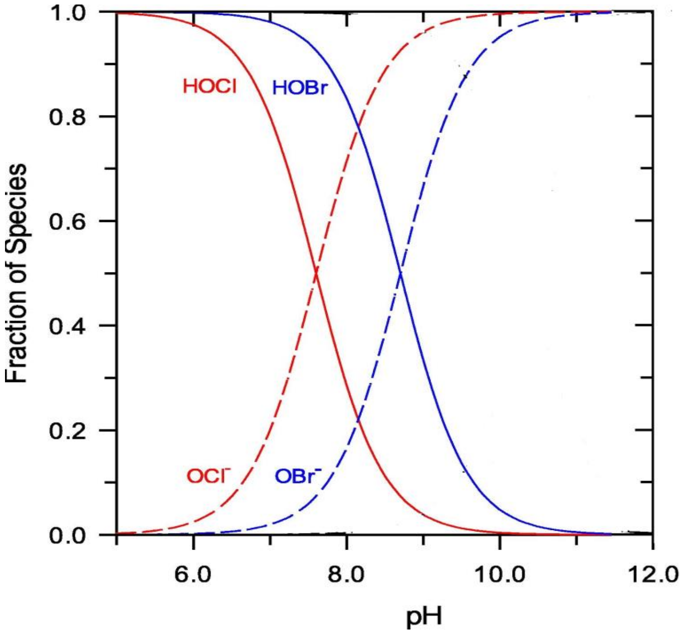


Figure 2. 2 The presence of HOBr, OBr^-, HOCl, and OCl^- as a function pH during water chlorination

As discussed earlier, the reactions between HOCl and ammonia present in water successively yields monochloramine (NH_2Cl), dichloramine ($NHCl_2$), trichloramine (NCl_3) and their bromo-analogue viz. NH_2Br, $NHBr_2$, and NBr_3 coexist when bromide is present [11,30]. Monobromamine and dibromamine are unstable and decay rapidly under the conditions encountered in water treatment [31]. Reactions and kinetics of oxidation of bromide and ammonia are presented in **Table 2. 1** to appreciate the occurrence of competitive fast-reactions during chlorination when both Br and ammonia are present. Scheme of the main reactions occurring during chlorination of water is depicted in **Figure 2. 3** (adopted from Allonier et al. (1999) [32]). Dissolved organic matter (DOM) is ubiquitous in natural water is a complex heterogeneous mixture of organic compounds with varying functional groups and molecular moiety such as aromatic, aliphatic, phenolic, and quinonic with varying molecular sizes [33]. The characterization of the ill-defined aquatic NOMs is extremely difficult due to the enormous complexity and heterogeneity of aquatic NOM [34]. NOM presence is undesirable when it comes to drinking water due to aesthetic, operational and economic factors [35]. Understanding of NOM's reactivity with chlorine and other disinfectant is critical for optimizing the water treatment processes, particularly concerning the formation of DBPs [36]. Reactivity of NOMs with disinfectant is affected by the physical and chemical character such as molecular weight [37], aromaticity [38], elemental composition and functional groups content [39]. Decrease in the chlorine reactivity order was reported as reduced sulfur components > primary and secondary amines > phenols and tertiary amines > double bonds, other aromatic components, carbonyls, amides by Deborde and Von Gunten (2008) [19]. Korshin et al. (2007) [40] has identified the polyhydroxy aromatic moieties as the major reactive sites in NOM, followed by esters and ketones. Natural organic matter (NOM) is the most complex mixture known and serve as the key determinant for the type and quantity of DBPs such as THMs and HAAs formation during water treatment processes [41,42] which is discussed later.

Table 2. 1 Apparent reaction rate constants of selected inorganic species with chlorine

Inorganic species	Rate constant (K) at pH 7(25^{0}C); ($M^{-1}s^{-1}$)	Arrhenius equation; K_{HOCl} ($M^{-1}s^{-1}$); T (^{0}K)	Refrences
Ammonia (NH_3)	1.3-1.8 * 10^4	K_{HOCl} = 5.4 * 10^9 exp(-2223/T); 6.6 * 10^8 exp(-1510/T)	[19], [30]
Monochloramine (NH_2Cl)	1.2-2.7 * 10^4	K_{HOCl} = 3.0 * 10^5 exp(-2210/T)	
Bromide	1.2-5.3 * 10^3	K_{HOCl}= 1.57 * 10^6 exp(1620/T)	

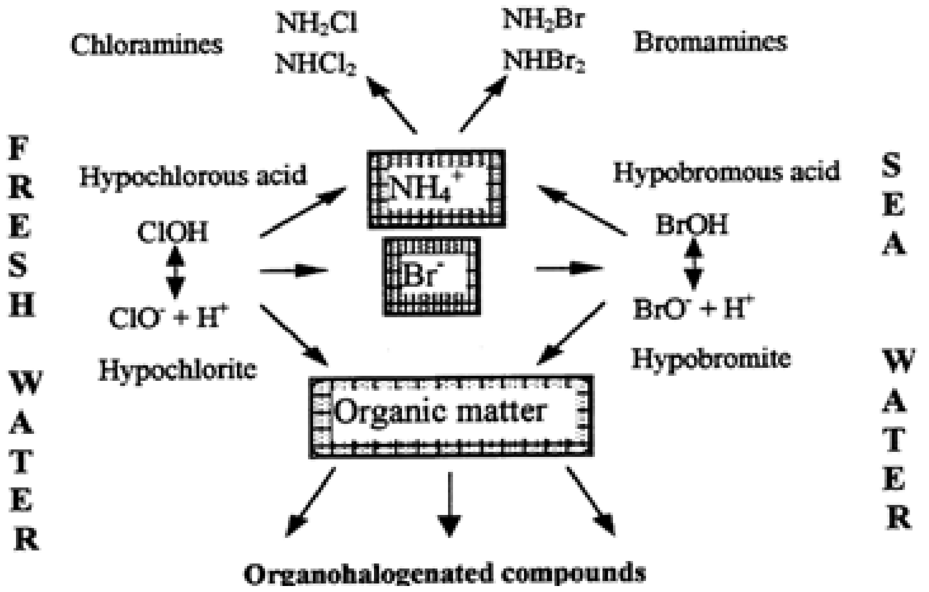


Figure 2. 3 Scheme of main reactions of chlorine in the presence of ammonia and bromide in natural water (adopted from Allonier et al. (1999) [32])

2.3 Aqueous Chemistry of Chlorine dioxide

Chlorine dioxide (ClO_2) is a molecular free radical, and in contrast to chlorine does not hydrolyze in water and exists as a dissolved gas in water at ambient temperatures. At concentrations greater than 10 g/L in solution, its vapor pressure reaches the explosive limit of 9.5% (ClO_2: air) and can poses explosion hazards [43]. However, as ClO_2 is usually used at dosages between 0.1 to 5 mg/L and this feature is not a major concern in water treatment utilities (Aieta and Berg 1986). ClO_2 is an unstable gas and highly soluble in aqueous solutions up to 20 g/l. Since it remains as dissolved gas in aqueous solutions, ClO_2 solution must be kept in closed containers to avoid volatile loss. Chlorine dioxide also loses its strength when exposed to ultraviolet light due to photolytic decomposition of ClO_2 to chlorate ion (ClO_3^-) [44,45]. Chlorine dioxide behaves as a selective oxidant through a one-electron transfer (eq. 2.9), and the oxidation-reduction reaction of ClO_2 occurs as follows [44,46,47]

$$\mathrm{ClO_2(aq) + e^- \rightarrow ClO_2^-\ (0.95\ V)} \qquad (2.9)$$

During water treatment, typically about 50-70% of chlorine dioxide disproportionate quickly to chlorite ion (ClO_2^-) and 0-10% to ClO_3^- which continually degrades in water according to the reactions as below [48,49]. Chlorite that is formed is less reactive than chlorine dioxide and gains four electrons to reduce to chloride and completes the reaction (eqs 2.10-2.11).

$$\mathrm{2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O} \qquad (2.10)$$

$$\mathrm{ClO_2^- + H^+ + 4e^- \rightarrow Cl^- + 2H_2O} \qquad (2.11)$$

Chlorine dioxide is often used as pre-oxidant combined with post chlorination in water treatment. Under these conditions, residual ClO_2 and ClO_2^- undergo side reactions with free chlorine to yield chlorate as shown in eqs (2.12-2.13). There is also evidence of reactions as in the below equations (2.14 and 2.15) [50] and reported to be accelerated in the presence of sunlight.

$$\mathrm{2ClO_2 + HOCl + H_2O \rightarrow 2ClO_3^- + 2H^+} \qquad (2.12)$$

$$\mathrm{2HOCl + ClO_2^- \rightarrow ClO_3^- + Cl_2 + H_2O} \qquad (2.13)$$

$$\mathrm{HOCl + 2ClO_2^- + H^+ \rightarrow 2ClO_2 + Cl^- + H_2O} \qquad (2.14)$$

$$\mathrm{2ClO_2 \rightarrow Cl_2 + 2O_2} \qquad (2.15)$$

Chlorine dioxide also reacts spontaneously with various inorganic substances such as Fe^{+2}, Mn^{+2}, S^{-2} present in water and get reduced to chloride. It also primarily reacts by oxidation with a variety of organic compound present in raw water to produce a number of volatile and nonvolatile organic compounds. In contrast, chlorine reacts not only via oxidation but also by electrophilic substitution to produce various chloro-organics. Unlike chlorine, chlorine dioxide is not known to react with ammonia to produce chloramines during water treatment [51]. From the redox potential of the chemical equilibriums **(Table 2. 2**) it appears that bromide cannot be oxidized by the chlorine dioxide-chlorite single electron transfer redox potential unlike ozone, chlorine, and hypochlorite [52]. However, Al-Otoum et al., (2016) [48] revealed that ClO_2 could oxidize bromide ion to HOBr which subsequently can take part in the usual halogen substitution reaction with NOMs present in natural water. According to the Nernst equation, the redox potential of ClO_2/ClO_2^- increases with ClO_2 concentration [53]. Thus, when chloride or bromide ion is present in a high concentration such as in seawater and at higher pH, which can be oxidized to HOCl or HOBr. HOCl generated by this way also further can oxidize instantaneously to HOBr if bromide is present [49].

Table 2. 2 Standard redox Potentials (E0) [52]

Reactions	Redox Potential, V
$\mathrm{HOCl} + \mathrm{H}^+ + 2\mathrm{e}^- \leftrightarrow \mathrm{Cl}^- + \mathrm{H_2O}$	1.49
$\mathrm{HOBr} + \mathrm{H}^+ + 2\mathrm{e}^- \leftrightarrow \mathrm{Br}^- + \mathrm{H_2O}$	1.33
$\mathrm{O_3} + \mathrm{H_2O} + 2\mathrm{e}^- \leftrightarrow \mathrm{O_2} + \mathrm{OH}^-$	1.24
$\mathrm{ClO_2(aq)} + \mathrm{e}^- \rightarrow \mathrm{ClO_2^-}$	0.95
$\mathrm{ClO_2^-} + \mathrm{H}^+ + 4\mathrm{e}^- \rightarrow \mathrm{Cl}^- + 2\mathrm{H_2O}$	0.78

2.4 Dissipation of chlorine and chlorine dioxide in water

2.4.1 Chlorine Decay

The fundamental requirement to study the issue of disinfectant decay equations is to use the derived decay constants to evaluate the disinfectant demand of the water, which varies with source water quality, temperature, pH and the material properties of water pipes [54,55]. In this discussion, the issue with the bulk decay of the chlorine and chlorine dioxide due to the constituents present in water is discussed, and wall decay resulting from the disinfectant interaction with the material properties of the flowing conduit is out of the preview of the discussion.

Dissolved organic matter, ammonia compounds, and reduced state inorganic materials such as Fe^{+2}, Mn^{+2}, S^{-2} are among the major constituents of water that react with chlorine and lead to its disappearance. In addition, chlorine decay also occurs due to due to thermal degradation, evaporation or photo-dissociation. The activity and availability of the above variable along with the water quality parameters such as pH, temperature influence the availability of the chlorine residual in water utilities. pH and temperature, which can both alter $HOCl/OCl^-$ equilibrium in water [56] or influence chemical reactions rate according to Arrhenius Law [57,58]. The impact of water quality on the efficacy of disinfection has been recognized for several decades, and conventionally, the influence of these variables has been the input for evaluation of chlorine decay kinetic [7,22,54,59–64]. Most of the chlorine decay models reported in the literature suggested either first-order or second-order kinetics. The first-order expression for the decay chlorine concentration in water, which do not consider the concentration of other species than chlorine in water can be expressed as follows [17,61]:

First order single constituent (chlorine) model

$$\mathrm{dC}/\mathrm{dt} + \mathrm{kC} = 0$$

Initial condition; C= C_0 at t=0

$$\int_{C0}^{Ct} \mathrm{dC}/\mathrm{C} = -\mathrm{kdt}$$

$$\mathrm{C_t} = \mathrm{C_0} * \mathrm{e}^{(-\mathrm{kt})}$$

n^th order single constituent (chlorine) model

$$\mathrm{dC}/\mathrm{dt} - \mathrm{k_n C^n} = 0$$

$$C = \left[k_n\, t\,(n-1) + \left({}^{1}\!/_{C_0}\right)^{n-1}\right]^{-1/_{n-1}}$$

For n=2 i.e 2nd order the above equation reduces to

$$C = C_0[1 + C_0 k_2 t]^{-1}$$

Where C_t: Chlorine concentration at time t

C_0: Initial chlorine concentration, and

and: are first-order and nth (n=2 for second order) order decay constant.

First-order kinetics has been used to describe chlorine decay in several models ignoring initial rapid reactions of chlorine with inorganic species [65–67]. A number of models made use of either first or second-order or with different kinetic parameters) to characterize the decay behavior during different time phase of reactions. Second-order chlorine decay model was developed based on the concept of competing reacting substances by Clark (1998) [68] and Boccelli et al. (2003) [69] taking into account "chlorine demand" as the second variable in their proposed 2nd order model. On the other hand, Hua et al. (1999) [64] proposed a semi-empirical combined first-order and second-order model. The decay processes were divided into various time range and decay models of first and second order were also proposed for each interval zone [70–72]. Conveniently, chlorine decay can be divided into two distinct phases; the first fast reactive 'initial chlorine decay' and the second, slower 'long-term decay' [73]. In an even more complex interpretation, the USEPA Water Treatment Plant model used zero-order for 0–5 min, second- order for 5 min-5 h and first order for time intervals greater than 5 h [17].

Two constituent decay model based and fast and slow reaction

$$aC_f + cC_s \overset{t=0}{\longrightarrow} C_0$$

$$\mathrm{aC_f} + Reactants \overset{k_f}{\rightarrow} products(1)$$

$$\mathrm{bC}_s + Reactants \overset{k_s}{\rightarrow} products(2)$$

Where, C_0, C_f, C_s are initial chlorine concentration, fraction of chlorine involved in fast reaction and fraction involved in fast reaction respectively; k_f and k_s are respective rates constant; a and b are stoichiometric coefficients. The above hypothesis was used to develop mathematical models for chlorine decay to calculate chlorine demand after a particular contact time.

Furthermore, it is well recognized that chlorine decay can be affected by a number of parameters such as organic content, inorganic content, pH, temperature, initial chlorine concentration, contact time, temperature resulting unpredictable chlorine demand of the water. Inorganic components in the natural water are derived from various minerals and other non-biological sources. As mentioned earlier their reaction with HOCl is generally fast and contribute to the instantaneous chlorine demand of the water [70]. It is well known that temperature affects a chemical reaction according to Van’t Hoff Arrhenius equation, and equally applicable for chlorine reaction with various constituents of water. Many authors have discussed the qualitative and quantitative impact of temperature on the chlorine reactions with various inorganic and organic constituents of the water [71,74,75]. pH alters chlorine speciation and reactivity of constituent of water significantly and hence can potentially influence the chlorine decay. However, water utilities largely operating in alkaline pH range, the effect of pH on chlorine decay was observed to be marginal [70]. Similarly, Zhang and Andrews [76] also observed no statistical difference in chlorine decay rates among samples treated at pH ranging from 6.6-8.6. Total organic carbon (TOC), UV absorbance at 254 nm (UVA_{254}), and specific UVA_{254} ($SUVA_{254}$)

are widely adopted surrogate to represent organic content in water and number of chlorine decay models considered as one of the significant variables.

2.4.2 Chlorine dioxide decay

As discussed above, several studies have addressed the issue of chlorine decay, whereas, studies so far on the chlorine dioxide decay is limited [77]. The similarity of chlorine dioxide decay behavior that with chlorine decay, not used historically as a primary disinfectant to maintain residual in water network, and its overall less common use compared to chlorine were the main reasons for the limited attention toward the studies on chlorine dioxide decay in water treatment. Like chlorine, chlorine dioxide decay occurs due to auto-decomposition reactions, reactions with organic and inorganic constituent present in the water, and surface interaction with the material and deposits in the flow circuit. However, unlike chlorine, chlorine dioxide is a selective oxidant primarily react through oxidation. As mentioned in the previous section, ClO_2 does not react with ammonia as chlorine does, cannot oxidize bromide at the ease that chlorine does, does not react with the way and the extent that chlorine reacts with wide range of organic matters, does not get hydrolyze in water and its relatively pH independent oxidant efficiency in the typical range of pH in water treatment are the most important features that differentiate it from that of chlorine. Photolytic decomposition of chlorine dioxide [44] and the instant redox reactions with natural organic matter are foremost in the decay of chlorine dioxide in water treatment [78]. Under typical water treatment conditions, chlorite and chlorate ion is generally the primary product constituting approximately 50 to 70% and 0-10% respectively [78,79]. The distribution of chlorite and chlorate is influenced by pH and sunlight. Ultraviolet light and even fluorescent lights can lead to photolysis [80]. Numerous inorganic and biological materials found in raw water react with chlorine dioxide [81]. Similar to chlorine decay, the concentration and types of various chemical and biological constituents lead to chlorine dioxide demand, as well as the temperature variance would impact the chlorine dioxide decay coefficient during water treatment. The decay coefficient for specific water can thus be different. Based on the order of the reaction, the mathematical form for alternative decay models can be proposed as reported by many investigators [65,82–85]. In a recent study, Ammar et al. (2014) [77] proposed a first-order kinetic model for the determination of the decay rate to predict chlorine dioxide residual.

2.5 Formation of disinfection by-products

Disinfection by-products (DBPs) are an unintended consequence of using disinfectants during water treatment. Since the discovery of chloroform and other trihalomethanes in 1974, more than 700 confirmed DBPs species have been reported in the literature so far [86,87]. However, with the existing analytical techniques available, still, more than 50% of the DBPs remains unidentified [88]. Approximately 50% of the total organic halides (TOX) formed during the chlorination of water is still not accounted for [87]. The inherent complexity of natural organic matters and analytical limitations particularly for highly polar and macromolecular DBPs are the major obstacle to identify the whole spectrum of DBPs formed during water treatment [89,90]. Even among the identified DBPs, toxicological studies have been carried out for only about 100 of them [90]. The concentrations of each group and each species in that group of DBPs vary according to both water source and type of disinfectant treatment. Studies have shown that the largest fraction of DBP to be found in treated water are THMs accounting for approximately 50% of all halogenated DBPs. HAAs, with their concentration on average being half that of THMs is the next largest fraction [91–93]. As the studies envisaged in this dissertation primarily focused on THMs, and HAAs formation, the subsequent review will emphasis on these two DBPs class.

2.5.1 Trihalomethanes

Trihalomethanes (THMs) with the general formula CHX_3 (X: Cl, Br) consists of chloroform ($CHCl_3$), dichlorobromomethanes ($CHCl_2Br$), bromodichloromethane ($CHClBr_2$) and Bromoform ($CHBr_3$). THMs result from reactions between chlorine or bromine and natural organic matter present in the water via the “classical” haloform reaction mechanism [94,95]. The general reaction can be expressed as follows:

HOCl + Br - + NOMs → THMs and other Halogenated DBPs

The proposed pathways proceed through fast electrophilic chlorination of ortho-carbon atom adjacent to hydroxyl or phenoxide ion in an alkaline medium as depicted in **Figure 2. 4**. After the aromatic ring is opened, bond breaking at tertiary halogenated carbon atom results in the formation of THMs. Bond breaking at different positions such as at “b” results into the formation of HAAs. The extent of halogenation and type of halogenating agents such as HOCl or HOBr dictates the distribution of various species.

Similarly, NOMs constituents containing oxygenated functional groups such as β-diketones undergo halogen substitution at the activated sites of carbon atom followed by rapid hydrolysis resulting in halogen substituted mono-ketones. If the “R” group attached to C=O carbon is a –OH, the reaction ends and DCAA is the resultant product. Otherwise, the intermediate products will be further halogenated according to to the scheme shown in **Figure 2. 5** to give THMs or HAAs [96]. THMs are relative to extremely volatile and slightly water soluble, with a solubility of less than 1 mg/ml at 25 °C [97]. The distribution of four species of THM varies according to water source characteristics, nature of disinfectant and operating conditions at the utilities. The key factors that majorly influence THM formation are pH, temperature, type and concentration of NOMs, bromide concentration, free chlorine concentration and contact time [21,98]. In most freshwater systems such as river, reservoir, groundwater, and lakes chloroform is by far the most dominant THM species [99–103]. However, the presence of higher bromide concentrations can lead to a significant shift towards brominated THMs, as in the case of seawater where bromoform is the dominant THM species [104–108]. Although the practice of seawater chlorination or use of other disinfectant such as ClO_2 is not as universal as drinking water treatment [109]. It is commonly used to control the growth of biofilm on heat exchangers of condenser cooling system of thermal power stations including nuclear power stations [104,110], to reduce biofouling of membranes in desalination plants [111,112], to disinfect ballast water and to prevent diseases in marine aquaculture industries [113–115].

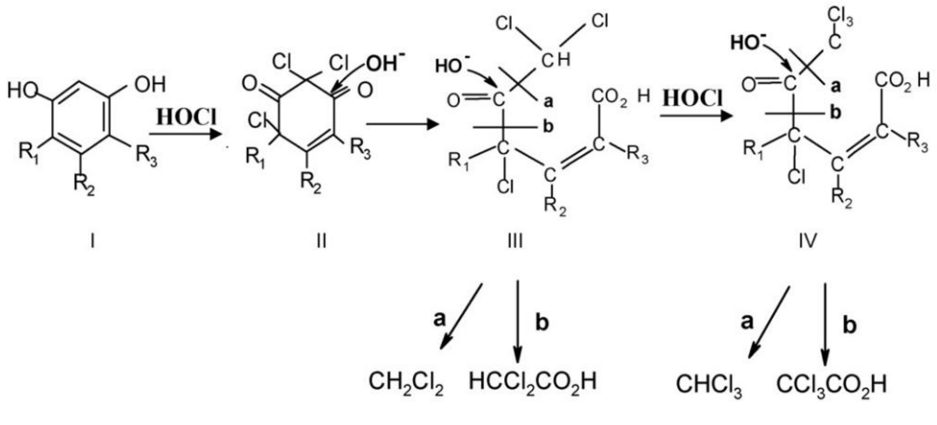
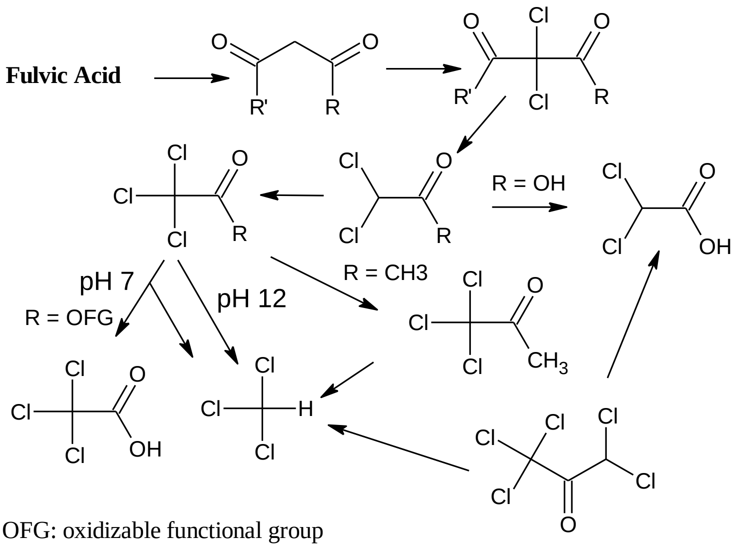


Figure 2. 4 Classical haloform reaction and other side reactions of HOCl with resorcinol moiety of natural organic matter (Adopted from Rook (1977) [94])



OFG: oxidizable functional group
Source: Adopted from Reckhow and Singer (1985)

Figure 2. 5 Conceptual reaction schemes for THMs and HAAs formation from fulvic acids (adopter from Reckhow and Singer (1985)[96])

Similar to HOCl and OCl$^-$, both HOBr and OBr$^-$ react with NOMs to form brominated and mixed chloro-bromo disinfection by-products. Although chlorine is more reactive than bromine (having an electronegativity value of 3.16 in comparison to 2.96 on the Pauling scale), HOBr is about 25 times more reactive than its counterpart HOCl [47]. The distribution of brominated THMs is a function of the Br_2: NOM ratio and Br_2: Cl_2 ratio [116]. Brominated organic by-products are suspected to be more harmful to health than their chlorinated analog [117–119]. For example, BDCM has been reported to pose a higher cancer risk than TCM [91], and the risk of rectal cancer has been shown recently to be associated specifically with levels of bromoform [120]. Because of the higher toxicity of brominated DBPs than their chloro- counterpart, bromide incorporation during DBP formation and THM speciation have received more attention in the recent years [38,47,86,121,122]. Bromine incorporation factor (BIF), defined as the molar THM concentration as bromide divided by the total molar THM concentration [123], is generally used to describe THMs distribution that could be formed in the presence of bromine. A number of investigators have illustrated the effect of pH on the yield of THMs, and they have demonstrated that a higher pH leads to an increased formation of THMs [91,95,96,124,125]. Rook (1974) [124] and Trussel and Umphres (1978) [126] have suggested that THM formation involves a hydrolysis step that is facilitated due to the availability of more reactive sites on the precursor molecule at higher pH. Obolensky and Singer (2005) [127] found that the pH effect is not significant to all the DBPs classes or individual species in that class. They observed that, although increased pH resulted in enhanced $CHCl_3$ formation, the effect was limited on the brominated THMs. Thus, pH appeared to play a decisive role in the dominance of DBPs such as THMs and HAAs in the chlorinated water [128,129]. Relatively, only a few studies have investigated the effect of temperature on DBP formation. As universally known, an increase in temperature increases the rate of reaction and so is in the case of DBP formation [130–133]. Engerholm and Amy (1983) [134] demonstrated that temperature not only increased the rate of formation but also increased the overall yield. Higher temperatures favor the rate of hydrolysis, which facilitates the breakup of the aromatic ring, making susceptible for further halogenation and a higher formation of DBPs [135]. Several investigators have observed increased THM formation during summer months which decreased in winters [91,136,137]. In addition to the direct effects of temperature, seasonal temperature variations can alter the characteristics and composition of organic precursors for DBPs formation [131,138,139]. It is reported that the presence of free chlorine is a prerequisite to THM formation and its yield increases with increasing chlorine dose and reaction time [95,140]. However, as the chlorine dose increases, the differential impact on increasing the rate of THM formation slows down and become insignificant when the chlorine dose applied is in sufficient excess of chlorine demand [126]. THM formation increases with increasing chlorine dosage up to a point until the reaction is limited by NOMs concentration. Singer (1994) [141] indicated that with an increasing chlorine dose and residual, the yield of haloaceticacids becomes greater than THM yield. A similar finding has been reported by Reckhow and Singer (1985) [96]. Depletion of free chlorine residual ceases formation of both THM and HAA, however, a limited amount of some other DBPs continues to form due to hydrolysis reactions [125,142].

2.5.2 Haloacetic acids

Haloacetic acids (HAAs) are carboxylic acids in which one or more hydrogen atoms of $–CH_3$ group of acetic acid are replaced with halogen atoms ($X_{1\text{-}3}H_{0\text{-}2}C\text{-}COOH$: X= Cl, Br). It consists of two monohaloacetic acids: $ClCH_2\text{-}COOH$, $BrCH_2\text{-}COOH$; three dihaloacetic acids: $Cl_2CH\text{-}COOH$, ClBr-COOH, $Br_2CH\text{-}COOH$; and four trihaloacetic acids: $Cl_3C\text{-}COOH$, $Cl_2BrC\text{-}COOH$, $Cl\text{-}Br_2C\text{-}COOH$, $Br_3C\text{-}COOH$. The conceptual mechanism of formation of HAAs during water disinfection as available in the literature is already shown in **Figure 2. 4** and **2. 5**. Among all the DBPs class formed, HAAs concentration on an average, is half of THMs and is the second largest fraction next to THMs during water disinfection [91–93,143]. The subset of total byproducts that have been identified constitutes only ∼30% of the total organic halogen (TOX) in chlorinated waters on a median basis, with THMs and HAAs each accounting for ∼10% of TOX [144]. HAAs being polar, it has high water solubility, and low Henry's constants mean that it can readily partitions into the water [145]. Once in the aquatic environment, it is not expected to partition into the atmosphere, making the systems most vulnerable to HAAs contamination [146]. Owing to their reproductive toxicity accompanied by carcinogenic and mutagenic effects, HAAs are of great concern to public health [147–150]. However, data availability on HAAs in water distribution system is much limited as compared to that of THMs [151]. The factors that affect the THM formation such as pH, temperature, disinfectant concentration, disinfectant type, reaction time, source water quality, etc. are all expected to affect HAAs formation, but might to varying extent [152]. Similar to THMs formation, HAAs formation also observed to be increased on increasing contact time. However, Chen and Weisel (1998) [153] found that though mean concentrations of THMs increased, concentrations of HAAs decreased with increasing residence time. The formation of haloacetic acids is pH-dependent; however, pH dependence formation of THMs is known more than HAAs [128]. Unlike in the case of THMs formation, a higher pH was associated with lower levels of some of the HAAs [91,154]. Obolensky and Singer (2008) [155] in their study with model compounds observed that trihaloacetic acids formation was inversely related to pH while dihaloacetic acids were not affected by pH changes. In a separate study, Cowman and Singer (1996) [156] found that elevated pH has a greater negative impact on brominated HAAs than on chlorinated HAAs. A study carried out by Shen et al. (2016) [157] on the effect of free chlorine, and organic load on HAAs formation demonstrated that monobromoacetic, tribromoacetic, chlordibromoacetic and trichloroacetic acid (HAAs) were found to be major DBP components formed. However, Cowman and Singer (1996) [156] observed that BCAA, BDCAA, and DBCAA are readily formed HAAs and constituted at least 10% of the total HAAs concentration in waters containing as little 0. mg/L bromide. In their study, mixed bromochloro- HAAs species were observed to be the major components of the total HAAs concentration at bromide concentrations found in raw drinking waters. Distribution of HAAs species among the mono-, di-, and trihalogenated forms appeared to be independent of bromide concentration [156]. Reckhow et al. (1990) [158] found that trihaloacetic acid (TCAA): THM ratio was higher in humic acid-rich water compared with fulvic acid-rich water. Naturally occurring organohalogens have been identified as the main precursors for brominated and chlorinated acetic acids in the marine and terrestrial environment [146,159]. Presently, many studies are focusing on the qualitative and quantitative aspects of HAAs during water treatment. Moreover, the high stability of some of the HAAs has prompted concern that their accumulation in surface waters would pose threats to humans and the ecosystem [150,160]. Marhaba and Van (2000) [161] investigated different NOM fractions such as hydrophilic and hydrophobic constituents and concluded that the hydrophilic fraction was the major precursor to the THM formation; whereas the hydrophobic fraction was the major precursor for HAAs.

2.6 Natural organic matter sources to water

Natural organic matter (NOM) is a mixture of organic compounds that occur universally in natural water. It is largely the remnant of microbial and abiotic reworking of organic matter originally derived from terrestrial or aquatic primary producers. Presence of NOMs is the basic cause for the formation of carbonaceous DBPs such as THMs and HAAs during water treatment [162,163]. NOMs in the aquatic system can be broadly divided into two functional fractions as humic and non-humic substances. Humic substances, which are composed of fulvic and humic acids, and non-humic substances, which include carbohydrates, hydrocarbons, lipids and amino acids [164,165]. It comprises a broad range of dissolved organic and is among the most complex molecular mixtures known [166]. In aquatic systems, dissolved organic matter is a mixture derived from biological processes in the system (autochthonous) and terrestrial organic matter transported from the surrounding environment (allochthonous) [167,168]. Catchment runoff and stream water generally have higher concentrations of DOM that are more aromatic and is also influenced by vegetation type [169]. For example, the highest NOM concentrations having been reported from catchments under forest cover, followed by grassland and then arable soils [170,171]. The highest concentration of DOC released into subsurface water, and lateral flows occur after the first major rainfall event demonstrating the importance of fresh litter material as NOM input [172]. NOMs have distinctive characteristics associated with the source from which it is originally derived (e.g., pedogenic: mainly terrestrial NOM derived from vegetation; aquagenic: largely from algae, bacteria, and other organism degradation and metabolites). For example, dissolved organic carbon (DOC) from aquatic algae is rich in nitrogen content and low in aromatic and phenolic carbon moiety. Whereas, NOM of terrestrial origin contains low nitrogen but high aromatic carbon and phenolic compounds. The distribution among each source is strongly dependent on climatological, hydrological and biogeochemical processes involved which also can alter the chemical structural and functional characteristics of the NOM. For instance, NOM in freshwater is often enriched in lignin-derived polyphenols that originate from vascular plant debris [173,174]. The abundance of these polyphenols renders the waters brown in color as typical for many rivers, lakes or wetlands. Marine DOM is comparably poor in these compounds [174,175]. It is widely recognized that phytoplankton is one of the main sources of organic matter in the sea contributing about 50 Gt/yr of organic carbon [176,177]. Heterotrophic bacteria play critical roles in carbon cycles in aquatic environments considered to be major contributors to the DOM pool in the ocean and even higher in coastal and freshwater environments [178]. Many studies demonstrated the ubiquitous nature of bacterially derived DOM in aquatic environments contributing to 20 to 40% of dissolved and particulate organic carbon [179,180]. It was indicated that bacterially derived organic matter could be a major source of organic matter in marine environments [178]. Moreover, because of the molecular complexity, full structural elucidation of aquatic DOM has not been possible to date [42]. A conceptual view of DOM composition along with their degradation and mixing through a series of biochemical reactions is presented in **Figure 2. 6** (adopted from Zark and Dittmar (2018) [42]). Whereas much attention has been paid by ecologists and hydrologists to decipher the origin, transport, and fate of organic carbon in natural waters [175,181,182] as well as to understand the origin of specific organic DBP precursor and their behavior which are still lacking [183]. Amphiphilic character of complex aquatic natural organic matter i.e., it contains both hydrophilic and hydrophobic component is one of the most important properties used for NOM classification with respect to their reactivity with disinfectant for DBP formation [184–187]. NOM found in natural water is generally hydrophobic acids, which make up approximately 50% of the DOC comprising of humic and fulvic acids [188]. The hydrophobic humic substances are generally regarded as the main cause of DBP formation [163], and it was observed that hydrophobic fraction produced more than two times the concentration of THMs that formed with hydrophilic acid fraction [189]. In contrast, Croue et al. (1993) [190] and Owen et al. (1993) [191] showed that the hydrophilic fractions were exerting the largest chlorine demand and greater THMs formation when compared to the hydrophobic material.

Many investigations related to DBPs formation and NOM content [192–194] concluded that an increase in the organic content in the water increases both the rate and the extent to which CBPs are formed. Because of the heterogeneity and difficulties of isolation into specific constituents, the amount of NOM is typically correlated to DBP formation through surrogate parameters such as total/dissolved organic carbon (TOC/DOC). Total organic contents cover a large array of compounds and therefore does not correlate well with CBPs formation [193], alternatively, UVA_{254} or $SUVA_{254}$ has been used as a measure of precursor concentration with varying success [158,162,195,196]. Recent research, aimed at improving the knowledge of precursor material, has attempted to identify relationships between individual components of NOM and DBPs formation [163,186]. Fractionation of natural organic matter into hydrophobic and hydrophilic constituents and their optical properties such as UV absorbance or fluorescence characters have been used to understand the NOM and DP formation relationships [184,197–200].

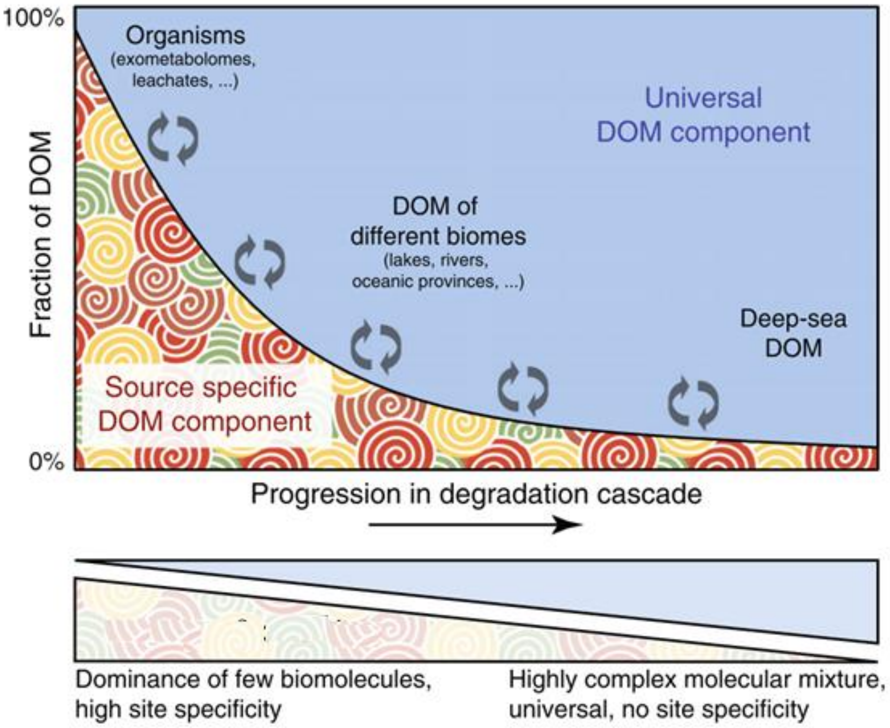


Figure 2. 6 Conceptual representation of DOM composition along the degradation and mixing in aquatic system (adopted from Zark and Dittmar (2018) [42])

2.7 Context of the present work

Because of the importance, many investigations have been directed towards the issue of disinfection by-products in the drinking and industrial water utilities throughout the world. Studies on monitoring and assessment of its load during water disinfection in various water utilities are important contributions to research in water treatment. Though India is having one of the largest water utilities network, study on the formation of disinfection by-products during water treatment is extremely scanty and sketchy, and the present work may be the first comprehensive studies involving various aspect of both THMs and HAAs formation for a Ph.D. dissertation in India. Moreover, studies on these are scarce for the real water sources, and almost nil from India in which the dissolved organic matters may have the distinct character as compared to that for water source of other geographic regions. Further, rarely CBPs formation has been assessed concurrently for different disinfectants such as Cl_2 and ClO_2 using different source water such as river, reservoir, and seawater that exist at the same location which might contain a blend of distinct, indistinguishable and unique organic matter mixture. Recently, chlorine dioxide has been increasingly used in place of chlorine for water disinfection worldwide due to its low organic reactivity to form lesser amount of carcinogenic chlorination by-products like THMs and HAAs. A major component of the present study addresses the formation of different DBPs class upon treatment of natural water with ClO_2 and Cl_2. Findings of the present study will give a clear and new insight on the formation of DBPs mainly THMs and HAAs acids during Cl_2 and ClO_2 treatment of water from different sources. The results of this study will provide crucial information which will help in taking decision to shift the disinfection practice from chlorination presently in vogue to chlorine dioxide. Moreover, the results presented in this dissertation fills the gap on the current information on the influence of the change in water sources on THMs and HAAs formation. In addition, the present study will also significantly contribute to the understanding on the effect of temporal variations in the water quality descriptors of different water sources on trihalomethanes formation, and how it is different from the conclusion derived from controlled laboratory conditions.

References

[1] G.C. White, The handbook of chlorination, Van Nostrand Reinhold Co, 1986.

[2] E.W. Akin, J.C. Hoff, E.C. Lippy, Waterborne outbreak control: which disinfectant?, Environ. Health Perspect. 46 (1982) 7–12.

[3] USEPA, Enhanced Coagulation and Enhanced precipitative Softenning Guidance Manual, (1999).

[4] E.M. Aieta, J.D. Berg, A Review of Chlorine Dioxide in Drinking Water Treatment, J. Am. Water Works Assoc. 78 (1986) 62–72.

[5] C.N. Haas, S.B. Karra, Kinetics of Wastewater Chlorine Demand Exertion, J. (Water Pollut. Control Fed. 56 (1999) 170–173.

[6] A.E. Griffin, Reaction of Heavy Doses of Chlorine in Various waters, J. AWAA. 31 (1939) 2121.

[7] B. Saunier, R.R. Selleck, Kinetics of Breakpoint Chlorination and of disinfection, Berkeley, CA, 1976.

[8] A.E. Griffin, N.S. Chamberlin, Some Chemical Aspects of Breakpoint Chlorination, J. New Engl. Water Work. Assoc. 55 (1941) 371–383.

[9] A.T. Palin, A Study of the Chloro Derivatives of Ammonia and Related compounds, With Special Reference to Their Formation in the Chlorination of Natural and Polluted Waters, Water Water Engg. 54 (1950) 151–256, 189–200, 248–256.

[10] R.L. Jolley, J.H. Carpenter, Aqueous chemistry of chlorine: Chemistry, analysis and fate of reactive oxidant species, 1 (1982).

[11] E. Agus, N. Voutchkov, D.L. Sedlak, Disinfection by-products and their potential impact on the quality of water produced by desalination systems: A literature review, Desalination. 237 (2009) 214–237.

[12] J.W.A. Charrois, S.E. Hrudey, Breakpoint chlorination and free-chlorine contact time: Implications for drinking water N-nitrosodimethylamine concentrations, Water Res. 41 (2007) 674–682.

[13] R.L. Wolfe, N.R. Ward, B.H. Olson, Interference in the bactericidal properties of inorganic chloramines by organic nitrogen compounds, Environ. Sci. Technol. 19 (1985) 1192–1195.

[14] I. Türetgen, Comparison of the Efficacy of Free Residual Chlorine and Monochloramine against Biofilms in Model and Full Scale Cooling Towers, Biofouling. 20 (2004) 81–85.

[15] R.A. Minear, G.L. Amy, eds., Disinfection By-Products in Water TreatmentThe Chemistry of Their Formation and Control, Lewis Publisher, Washington DC, 1996.

[16] J. Yoon, J.N. Jensen, Distribution of aqueous chlorine with nitrogenous compounds: chlorine transfer from organic chloramines to ammonia, Environ. Sci. Technol. 27 (1993) 403–409.

[17] B. Warton, A. Heitz, C. Joll, R. Kagi, A new method for calculation of the chlorine demand of natural and treated waters, Water Res. 40 (2006) 2877–2884.

[18] I.W. Wei, C.J. Moriss, Dynamic of break poiint chlorination, 1974.

[19] M. Deborde, U. von Gunten, Reactions of chlorine with inorganic and organic compounds during water treatment-Kinetics and mechanisms: A critical review, Water Res. 42 (2008) 13–51.

[20] V. Jegatheesan, S. Weragoda, C. Visvanathan, Rapid water quality characterization for chlorine demand and THM formation in drinking waters, J. Water Supply Res. Technol. 57 (2008) 259–272.

[21] M.P. Abdullah, L.F. Yee, S. Ata, A. Abdullah, B. Ishak, K.N.Z. Abidin, The study of interrelationship between raw water quality parameters, chlorine demand and the formation of disinfection by-products, Phys. Chem. Earth. 34 (2009) 806–811.

[22] S.K. Gang, D. C., Clevenger, T. E., & Banerji, Modeling Chlorine Decay in Surface Water, J. Environ. Informatics. 1 (2003) 21–27.

[23] G.T.F. Wong, T.J. Oatts, Dissolved organic matter and the dissipation of chlorine in estuarine water and seawater, Water Res. 18 (1984) 501–504.

[24] J.C. Goldman, H.L. Quinny, J.M. Capuzzo, Chlorine disappearance in sea-water, Water Res. 13 (1979) 315–323.

[25] J. Arotsky, M.C.R. Symons, Halogen cations, Q. Rev. Chem. Soc. 16 (1962) 282.

[26] D.P. Cherney, S.E. Duirk, J.C. Tarr, T.W. Collette, Monitoring the Speciation of Aqueous Free Chlorine from pH 1 to 12 with Raman Spectroscopy to Determine the Identity of the Potent Low-pH Oxidant, Appl. Spectrosc. 60 (2006) 764–772.

[27] G. Zimmerman, F.C. Strong, Equilibria and Spectra of Aqueous Chlorine Solutions, J. Am. Chem. Soc. 79 (1957) 2063–2066.

[28] E.A. Voudrias, M. Reinhard, A kinetic model for the halogenation of p-xylene in aqueous hypochlorous acid solutions containing chloride and bromide, Environ. Sci. Technol. 22 (1988) 1056–1062.

[29] G.C. White, Disinfection: Present and Future, J. Am. Water Works Assoc. 66 (1974) 689–690.

[30] R. Liu, C. Tian, C. Hu, Z. Qi, H. Liu, J. Qu, Effects of bromide on the formation and transformation of disinfection by-products during chlorination and chloramination, Sci. Total Environ. 625 (2018) 252–261.

[31] Hongxia Lei, and Benito J. Mariñas, R.A. Minear, Bromamine Decomposition Kinetics in Aqueous Solutions, (2004).

[32] A.S. Allonier, M. Khalanski, V. Camel, A. Bermond, Characterization of Chlorination By- products in Cooling Efluents of Coastal Nuclear Power Stations, Mar. Pollut. Bull. 38 (1999) 1232–1241.

[33] A. Baker, R.G.M. Spencer, Characterization of dissolved organic matter from source to sea using fluorescence and absorbance spectroscopy, Sci. Total Environ. 333 (2004) 217–232.

[34] J. Świetlik, E. Sikorska, Characterization of natural organic matter fractions by high pressure size-exclusion chromatography, specific UV absorbance and total luminescence spectroscopy, Polish J. Environ. Stud. 15 (2006) 145–153.

[35] AWWARF, Characterization of Natural Organic Matter in Drinking Water, (2000).

[36] S.E. Barrett, S.W. Krasner, G.L. Amy, American Chemical Society. Division of Environmental Chemistry., C. American Chemical Society. Meeting (217th : 1999 : Anaheim, Z. Zhang, S. Echigo, R.A. Minear, M.J. Plewa, S.E. Barrett, S.W. Krasner, G.L. Amy, Natural organic matter and disinfection by-products characterization and control in drinking water, American Chemical Society, 2000.

[37] S.E. Cabaniss, Q. Zhou, P.A. Maurice, Y.-P. Chin, G.R. Aiken, A Log-Normal Distribution Model for the Molecular Weight of Aquatic Fulvic Acids, (2000).

[38] P. Westerhoff, P. Chao, H. Mash, Reactivity of natural organic matter with aqueous chlorine and bromine, Water Res. 38 (2004) 1502–1513.

[39] E.M. Perdue, J.D. Ritchie, Dissolved Organic Matter in Freshwaters, in: Treatise on Geochemistry, Elsevier, 2003: pp. 273–318.

[40] G.V. Korshin, M.M. Benjamin, H.-S. Chang, H. Gallard, Examination of NOM Chlorination Reactions by Conventional and Stop-Flow Differential Absorbance Spectroscopy, (2007).

[41] C. Li, D. Wang, X. Xu, Z. Wang, Formation of known and unknown disinfection by-products from natural organic matter fractions during chlorination, chloramination, and ozonation, Sci. Total Environ. 587–588 (2017) 177–184.

[42] M. Zark, T. Dittmar, Universal molecular structures in natural dissolved organic matter, Nat. Commun. 9 (2018) 3178.

[43] R.Y. Jin, S.-Q. Hu, Y.-G. Zhang, T. Bo, Concentration-dependence of the explosion characteristics of chlorine dioxide gas, J. Hazard. Mater. 166 (2009) 842–847.

[44] USEPA, Alternatives disinfectants and oxidants - Guidance manual, (1999) 346.

[45] J. Huang, L. Wang, N. Ren, F. Ma, Juli, Disinfection effect of chlorine dioxide on bacteria in water, Water Res. 31 (1997) 607–613.

[46] G. Petrucci, M. Rosellini, Chlorine dioxide in seawater for fouling control and post-disinfection in potable waterworks, Desalination. 182 (2005) 283–291.

[47] C.Y. Chang, Y.H. Hsieh, Y.M. Lin, P.Y. Hu, C.C. Liu, K.H. Wang, The organic precursors affecting the formation of disinfection by-products with chlorine dioxide, Chemosphere. 44 (2001) 1153–1158.

[48] F. Al-Otoum, M.A. Al-Ghouti, T.A. Ahmed, M. Abu-Dieyeh, M. Ali, Disinfection by-products of chlorine dioxide (chlorite, chlorate, and trihalomethanes): Occurrence in drinking water in Qatar, Chemosphere. 164 (2016) 649–656.

[49] J. Han, X. Zhang, J. Liu, X. Zhu, T. Gong, Characterization of halogenated DBPs and identification of new DBPs trihalomethanols in chlorine dioxide treated drinking water with multiple extractions, J. Environ. Sci. 58 (2017) 83–92.

[50] W. Gan, H. Huang, X. Yang, Z. Peng, G. Chen, Emerging investigators series: Disinfection by-products in mixed chlorine dioxide and chlorine water treatment, Environ. Sci. Water Res. Technol. 2 (2016) 838–847.

[51] S.A. Hubbs, D. Amundsen, P. Olthius, Use of chlorine dioxide, chloramines, and short-term free chlorination as alternative disinfectants, J. Am. Water Works Assoc. 73 (1981) 97–101.

[52] M. Belluati, E. Danesi, G. Petrucci, M. Rosellini, Chlorine dioxide disinfection technology to avoid bromate formation in desalinated seawater in potable waterworks, Desalination. 203 (2007) 312–318.

[53] T. Reemtsma, M. Jekel, Wiley InterScience (Online service), Organic pollutants in the water cycle : properties, occurrence, analysis and environmental relevance of polar compounds, Wiley-VCH, 2006.

[54] A.O.O. Al-Jasser, Chlorine decay in drinking-water transmission and distribution systems: Pipe service age effect, Water Res. 41 (2007) 387–396.

[55] B. Politechnika Wrocławska., D. Kowalski, A. Musz, Chlorine decay in water distribution systems, Environ. Prot. Eng. Vol. 32 (2006) 5–16.

[56] J.C. Morris, The Mechanism of the Hydrolysis of Chlorine, J. Am. Chem. Soc. 68 (1946) 1692–1694.

[57] G.B. Wickramanayake, A.J. Rubin, O.J. Sproul, Inactivation of Naegleria and Giardia Cysts in Water by Ozonation, J. (Water Pollut. Control Fed. 56 (1984) 983–988.

[58] J.L. Rennecker, B.J. Mariñas, J.H. Owens, E.W. Rice, Inactivation of Cryptosporidium parvum oocysts with ozone, Water Res. 33 (1999) 2481–2488.

[59] P. Biswas, C. Lu, R.M. Clark, A model for chlorine concentration decay in pipes, Water Res. 27 (1993) 1715–1724.

[60] B. Barbeau, R. Desjardins, C. Mysore, M. Prévost, M. Preost, Impacts of water quality on chlorine and chlorine dioxide efficacy in natural waters, Water Res. 39 (2005) 2024–2033.

[61] F. Nejjari, V. Puig, R.Pérez, J. Quevedo, M.A. Cugueró, G. Sanz, J.M. Mirats, Chlorine Decay Model Calibration and Comparison: Application to a Real Water Network, Procedia Eng. 70 (2014) 1221–1230.

[62] K.K. Satpathy, K.V.K. Nair, P.K. Mathur, Chlorine demand & chemical control of biofouling in power plant cooling system, in: M.P. Thompson, R. Nagabhushanam (Eds.), Recent Dev. Biofouling Control, Oxford Oxford & IBH Publishing Company, New Delhi, 1994: pp. 397–407.

[63] S.B. Murphy, Modeling chlorine concentrations in municipal water systems, (1985).

[64] F. Hua, J. West, R. Barker, C. Forster, Modelling of chlorine decay in municipal water supplies, Water Res. 33 (1999) 2735–2746.

[65] P.F. Vasconcelos, J.J., Boulos, R.M. Clark, Kinetics of chlorine decay, J. Am. Water Work. Assoc. 89 (1997) 54–65.

[66] D.D. Gang, R.S. Jr., T.E. Clevenger, S.K. Banerji, Using chlorine demand TO PREDICT TTHM and HAA9 formation, J. Am. Water Works Assoc. 94 (2002) 76–86.

[67] L.A. Rossman, R.M. Clark, W.M. Grayman, Modeling Chlorine Residuals in Drinking-Water Distribution Systems, J. Environ. Eng. 120 (1994) 803–820.

[68] R.M. Clark, Chlorine Demand and TTHM Formation Kinetics: A Second-Order Model, J. Environ. Eng. 124 (1998) 16–24.

[69] D.L. Boccelli, M.E. Tryby, J.G. Uber, R.S. Summers, A reactive species model for chlorine decay and THM formation under rechlorination conditions, Water Res. 37 (2003) 2654–2666.

[70] W. Sung, J. Levenson, T. Toolan, D. Kelly O'day, Chlorine Decay Kinetics a Reservoir Water, J. Am. Water Work Assoc. (2001) 101–110.

[71] A. Jadas-Hécart, A. El Morer, M. Stitou, P. Bouillot, B. Legube, Modelisation de la demande en chlore d'une eau traitee, Water Res. 26 (1992) 1073–1084.

[72] R.M. Clark, M. Sivaganesan, Predicting Chlorine Residuals in Drinking Water: Second Order Model, J. Water Resour. Plan. Manag. 128 (2002) 152–161.

[73] R.G. Qualls, J.D. Johnson, Kinetics of the short-term consumption of chlorine by fulvic acid, Environ. Sci. Technol. 17 (1983) 692–698.

[74] H. Gallard, U. Von Gunten, Chlorination of natural organic matter: Kinetics of chlorination and of THM formation, Water Res. 36 (2002) 65–74.

[75] P. Viera, S.T. Coelho, D. Loureiro, Accounting for the influence of initial chlorine concentration, TOC, iron and temperature when modelling chlorine decay in water supply, Ournal Water Supply Res. Technol. 53 (2004) 453–467.

[76] H. Zhang, S.A. Andrews, Catalysis of copper corrosion products on chlorine decay and HAA formation in simulated distribution systems, Water Res. 46 (2012) 2665–2673.

[77] T.A. Ammar, K.Y. Abid, A.A. El-Bindary, A.Z. El-Sonbati, Chlorine dioxide bulk decay prediction in desalinated drinking water, Desalination. 352 (2014) 45–51.

[78] K.S. Werdehoff, P.C. Singer, Chlorine Dioxide Effects on THMFP, TOXFP, and the Formation of Inorganic By-products, J. Am. Water Works Assoc. 79 (1987) 107–113.

[79] C. Rav-Acha, A. Serri, E. (Goldstein) Choshen, B. Limoni, Disinfection of Drinking Water Rich in Bromide with Chlorine and Chlorine Dioxide, While Minimizing the Formation of Undesirable By-Products, Water Sci. Technol. 17 (1985) 611–621.

[80] W.J. Cooper, A.C. Jones, R.F. Whitehead, R.G. Zika, R.G. Petasne, Sunlight Induced Photochemical Decay of Oxidants in Natural Waters: Implications in Ballast Water Treatment, 2006.

[81] R.L. Jolley, Electric Power Research Institute., Water chlorination : volume 5 : chemistry, environmental impact and health effects : proceedings of the Fifth Conference on Water Chlorination: Environmental Impact and Health Effects, Williamsburg, Virginia, June 3-8, 1984, Lewis, 1985.

[82] I. Fisher, G. Kastl, A. Sathasivan, A suitable model of combined effects of temperature and initial condition on chlorine bulk decay in water distribution systems, Water Res. 46 (2012) 3293–3303.

[83] J.C. Powell, N.B. Hallam, J.R. West, C.F. Forster, J. Simms, Factors Which Control Bulk Chlorine Decay Rates, Water Res. 34 (2000) 117–126.

[84] I. Fisher, G. Kastl, A. Sathasivan, Evaluation of suitable chlorine bulk-decay models for water distribution systems, Water Res. 45 (2011) 4896–4908.

[85] A. Jabari Kohpaei, A. Sathasivan, Chlorine decay prediction in bulk water using the parallel second order model: An analytical solution development, Chem. Eng. J. 171 (2011) 232–241.

[86] N. Ates, S.S. Kaplan, E. Sahinkaya, M. Kitis, F.B. Dilek, U. Yetis, Occurrence of disinfection by-products in low DOC surface waters in Turkey, J. Hazard. Mater. 142 (2007) 526–534.

[87] S.D. Richardson, M.J. Plewa, E.D. Wagner, R. Schoeny, D.M. Demarini, Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research Antioch-226, (2007).

[88] S.D. Richardson, C. Postigo, Formation of DBPs: State of the Science, 2015 : pp. 189–214.

[89] E.E. Lavonen, M. Gonsior, L.J. Tranvik, P. Schmitt-Kopplin, S.J. Köhler, Selective Chlorination of Natural Organic Matter: Identification of Previously Unknown Disinfection Byproducts, Environ. Sci. Technol. 47 (2013) 2264–2271.

[90] J. Han, X. Zhang, Evaluating the Comparative Toxicity of DBP Mixtures from Different Disinfection Scenarios: A New Approach by Combining Freeze-Drying or Rotoevaporation with a Marine Polychaete Bioassay, Environ. Sci. Technol. 52 (2018) 10552–10561.

[91] S.W. Krasner, M.J. McGuire, J.G. Jacangelo, N.L. Patania, K.M. Reagan, E.M. Aieta, The Occurrence of Disinfection By-products in US Drinking Water, J. Am. Water Works Assoc. 81 (1989) 41–53.

[92] S. Lee, H. Guo, S.M. Lam, S.L. Lau, Multipathway risk assessment on disinfection by-products of drinking water in Hong Kong, Environ. Res. 94 (2004) 47–56.

[93] E.C. Nieminski, S. Chaudhuri, T. Lamoreaux, The Occurrence of DBPs in Utah Drinking Waters, J. Am. Water Works Assoc. 85 (1993) 98–105.

[94] J.J. Rook, Chlorination reactions of fulvic acids in natural waters, Environ. Sci. Technol. 11 (1977) 478–482.

[95] A. Adin, J. Katzhendler, D. Alkaslassy, C. Rav-Acha, Trihalomethane formation in chlorinated drinking water: A kinetic model, Water Res. 25 (1991) 797–805.

[96] D.A. Reckhow, P.C. Singer, Mechanisms of organic halide formation during fulvic acid chlorination and implications with respect to preozonation, in: R.L. Jolley, H. Gorcher, D.H. Hamilton (Eds.), Water Chlorination Environ. Impact Heal. Eff., Ann Arbor Science, 1985: pp. 1229–1257.

[97] WHO, Trihalomethanes in drinking water: Background document for development of WHO Guidelines for Drinking-water Quality, J. Toxicol. Environ. Health. A. 73 (2005).

[98] C. Cortés, R. Marcos, Genotoxicity of disinfection byproducts and disinfected waters: A review of recent literature, Mutat. Res. Toxicol. Environ. Mutagen. 831 (2018) 1–12.

[99] R.E. Rathbun, Speciation of trihalomethane mixtures for the Mississippi, Missouri, and Ohio Rivers, Sci. Total Environ. 180 (1996) 125–135.

[100] A. Szczuka, K.M. Parker, C. Harvey, E. Hayes, A. Vengosh, W.A. Mitch, Regulated and unregulated halogenated disinfection byproduct formation from chlorination of saline groundwater, Water Res. 122 (2017) 633–644.

[101] J.C. Yu, L. nor Cheng, Speciation and distribution of trihalomethanes in the drinking water of Hong Kong, Environ. Int. 25 (1999) 605–611.

[102] M.J. Rodriguez, Y. Vinette, J.B. Sérodes, C. Bouchard, Trihalomethanes in drinking water of greater Quebec region (Canada): Occurrence, variations and modelling, Environ. Monit. Assess. 89 (2003) 69–93.

[103] D. Baytak, A. Sofuoglu, F. Inal, S.C. Sofuoglu, Seasonal variation in drinking water concentrations of disinfection by-products in IZMIR and associated human health risks, Sci. Total Environ. 407 (2008) 286–296.

[104] H.A. Jenner, C.J.L. Taylor, M. Van Donk, M. Khalanski, Chlorination by-products in chlorinated cooling water of some European coastal power stations, Mar. Environ. Res. 43 (1997) 279–293.

[105] A. Abdel-Wahab, Formation of Trihalomethanes during Seawater Chlorination, J. Environ. Prot. (Irvine,. Calif). 01 (2010) 456–465.

[106] T. Manasfi, M. De Méo, B. Coulomb, C. Di Giorgio, J-L. Boudenne, Identification of disinfection by-products in freshwater and seawater swimming pools and evaluation of genotoxicity, Environ. Int. 88 (2016) 94–102.

[107] D. Boudjellaba, J. Dron, G. Revenko, C. Demelas, J.L. Boudenne, Chlorination by-product concentration levels in seawater and fish of an industrialised bay (Gulf of Fos, France) exposed to multiple chlorinated effluents, Sci. Total Environ. 541 (2016) 391–399.

[108] N.M. Ram, Y.G. Mussalli, C. Winston, Total Trihalomethane Formation during Targeted and Conventional Chlorination of Seawater for Biofouling Control, Res. J. Water Pollut. Control Fed. 62 (1990) 789–795.

[109] M. Fabbricino, G. V. Korshin, Formation of disinfection by-products and applicability of differential absorbance spectroscopy to monitor halogenation in chlorinated coastal and deep ocean seawater, Desalination. 176 (2005) 57–69.

[110] I. Stemmler, I. Hense, B. Quack, Marine sources of bromoform in the global open ocean-global patterns and emissions, Biogeosciences. 12 (2015) 1967–1981.

[111] A.G.I. Dalvi, R. Al-Rasheed, M.A. Javeed, Haloacetic acids (HAAs) formation in desalination processes from disinfectants, Desalination. 129 (2000) 261–271.

[112] Z. Yang, Y.X. Sun, T. Ye, N. Shi, F. Tang, H.Y. Hu, Characterization of trihalomethane, haloacetic acid, and haloacetonitrile precursors in a seawater reverse osmosis system, Sci. Total Environ. 576 (2017) 391–397.

[113] R. Xue, H. Shi, Y. Ma, J. Yang, B. Hua, E.C. Inniss, C.D. Adams, T. Eichholz, Evaluation of thirteen haloacetic acids and ten trihalomethanes formation by peracetic acid and chlorine drinking water disinfection, Chemosphere. 189 (2017) 349–356.

[114] F.X. Simon, E. Berdalet, F.A. Gracia, F. Espana, J. Llorens, Seawater disinfection by chlorine dioxide and sodium hypochlorite. A comparison of biofilm formation, Water. Air. Soil Pollut. 225 (2014).

[115] H. Zhang, H. Dong, C. Adams, Z. Qiang, G. Luan, L. Wang, Formation and speciation of disinfection byproducts during chlor(am)ination of aquarium seawater, J. Environ. Sci. 33 (2015) 116–124.

[116] R.S. Summers, M.A. Benz, H.M. Shukairy, L. Cummings, Effect of Separation Processes on the Formation of Brominated THMs, J. Am. Water Works Assoc. 85 (1993) 88–95.

[117] T. Nobukawa, S. Sanukida, Effect of bromide ions on genotoxicity of halogenated by-products from chlorination of humic acid in water., Water Res. 35 (2001) 4293–8.

[118] S.W. Krasner, C.F.T. Lee, R. Chinn, S. Hartono, H.S. Weinberg, S.D. Richardson, J. Pressman, T.F. Speth, R. Miltner, J.E. Simmons, Bromine incorporation in regulated and emerging DBPs and the relative predominance of mono-, di-, and trihalogenated DBPs, Proc. AWWA WQTC. Denver, Color. AWWA. (2008) 1–16.

[119] S.D. Richardson, Disinfection by-products and other emerging contaminants in drinking water, TrAC Trends Anal. Chem. 22 (2003) 666–684.

[120] G.E. Bove, P.A. Rogerson, J.E. Vena, J.E. Vena, Case control study of the geographic variability of exposure to disinfectant byproducts and risk for rectal cancer., Int. J. Health Geogr. 6 (2007) 18.

[121] C.J. Nokes, E. Fenton, C.J. Randall, Modelling the formation of brominated trihalomethanes in chlorinated drinking waters, Water Res. 33 (1999) 3557–3568.

[122] J. Sohn, G. Amy, Y. Yoon, Bromide ion incorporation into brominated disinfection by-products, Water. Air. Soil Pollut. 174 (2006) 265–277.

[123] J.P. Gould, L.E. Fitchhorn, E. Urheim, Formation of brominated trihalomethanes: extent and kinetics, in: Pro-Ceedings 4th Conf. Water Chlorination, Ann Arbor Science, 1981: pp. 297–310.

[124] J.J. Rook, Formation of haloforms during chlorination of natural waters, J. Water Treat. Exam. 23 (1974) 234–243.

[125] L. Liang, P.C. Singer, Factors Influencing the Formation and Relative Distribution of Haloacetic Acids and Trihalomethanes in Drinking Water, Environ. Sci. Technol. 37 (2003) 2920–2928.
[126] R.R. Trussell, M.D. Umphres, The Formation of Trihalomethanes, J. Am. Water Works Assoc. 70 (1978) 604–612.
[127] A. Obolensky, P.C. Singer, Halogen Substitution Patterns among Disinfection Byproducts in the Information Collection Rule Database, Environ. Sci. Technol. (2005) 2719–2730.
[128] Y.-C. Hung, B.W. Waters, V.K. Yemmireddy, C.-H. Huang, pH effect on the formation of THM and HAA disinfection byproducts and potential control strategies for food processing, J. Integr. Agric. 16 (2017) 2914–2923.
[129] K.M.S. Hansen, S. Willach, M.G. Antoniou, H. Mosbæk, H.-J. Albrechtsen, H.R. Andersen, Effect of pH on the formation of disinfection byproducts in swimming pool water - Is less THM better?, Water Res. 46 (2012) 6399–409.
[130] M.C. Kavanaugh, A.R. Trussell, J. Cromer, R.R. Trussell, An Empirical Kinetic Model of Trihalomethane Formation: Applications to Meet the Proposed THM Standard, J. Am. Water Works Assoc. 72 (1980) 578–582.
[131] I. Toroz, V. Uyak, Seasonal variations of trihalomethanes (THMs) in water distribution networks of Istanbul City, Desalination. 176 (2005) 127–141.
[132] M.J. Rodriguez, J.B. Sérodes, Spatial and temporal evolution of trihalomethanes in three water distribution systems., Water Res. 35 (2001) 1572–1586.
[133] J. Kim, Y. Chung, D. Shin, M. Kim, Y. Lee, Y. Lim, D. Lee, Chlorination by-products in surface water treatment process, Desalination. 151 (2002) 1–9.
[134] B.A. Engerholm, G.L. Amy, A predictive model for chloroform formation from humic acid, J. Am. Water Works Assoc. 75 (1983) 418–423.
[135] I. Garcia, Removal of natural organic matter by enhanced coagulation in Nicaragua, Stockholm University, Sweden, 2005.
[136] M.R. Roberts, Trihalomethane Management in Water Supply, The University of Birmingham, 2004.
[137] M.J. Rodriguez, J.B. Sérodes, Spatial and temporal evolution of trihalomethanes in three water distribution systems., Water Res. 35 (2001) 1572–1586.
[138] M.J. Rodriguez, J.B. Sérodes, P. Levallois, F. Proulx, Chlorinated disinfection by-products in drinking water according to source, treatment, season, and distribution location, J. Environ. Eng. Sci. 6 (2007) 355–365.
[139] V. Uyak, K. Ozdemir, I. Toroz, Seasonal variations of disinfection by-product precursors profile and their removal through surface water treatment plants, Sci. Total Environ. 390 (2008) 417–424.
[140] M.A. El-Dib, R.K. Ali, THMs formation during chlorination of raw Nile River water, Water Res. 29 (1995) 375–378.
[141] P.C. Singer, Control of Disinfection By-Products in Drinking Water, J. Environ. Eng. 120 (1994) 727–744.
[142] A. Grunwald, A.D. Nikolaou, S.K. Golfinopoulos, T.D. Lekkas, Formation of organic by-products during chlorination of natural waters., J. Environ. Monit. 4 (2002) 910–916.
[143] M.J. Rodriguez, J. Serodes, D. Roy, Formation and fate of haloacetic acids (HAAs) within the water treatment plant, (2007).
[144] X.-F. Li, W.A. Mitch, Drinking Water Disinfection Byproducts (DBPs) and Human Health Effects: Multidisciplinary Challenges and Opportunities, Environ. Sci. Technol. 52 (2018) 1681–1689.
[145] D. Bowden, S. Clegg, P. Brimblecombe, The Henry's law constant of trifluoroacetic acid and its partitioning into liquid water in the atmosphere, Chemosphere. 32 (1996) 405–420.

[146] M.L. Hanson, K.R. Solomon, Haloacetic acids in the aquatic environment. Part I: macrophyte toxicity, Environ. Pollut. 130 (2004) 371–383.

[147] G.M. Nelson, A.E. Swank, L.R. Brooks, K.C. Bailey, S.E. George, Metabolism, microflora effects, and genotoxicity in haloacetic acid-treated cultures of rat cecal microbiota., Toxicol. Sci. 60 (2001) 232–41.

[148] IPSC, Disinfectants and disinfectatnts byproducts, Environmental Health Criteria 216, Geneva, 2000.

[149] M.J. Nieuwenhuijsen, M.B. Toledano, N.E. Eaton, J. Fawell, P. Elliott, Chlorination disinfection byproducts in water and their association with adverse reproductive outcomes: a review., Occup. Environ. Med. 57 (2000) 73–85.

[150] P. Pavelic, B.C. Nicholson, P.J. Dillon, K.E. Barry, Fate of disinfection by-products in groundwater during aquifer storage and recovery with reclaimed water., J. Contam. Hydrol. 77 (2005) 351–73.

[151] E. Malliarou, C. Collins, N. Graham, M.J. Nieuwenhuijsen, Haloacetic acids in drinking water in the United Kingdom, Water Res. 39 (2005) 2722–2730.

[152] Report on Carcinogens Monograph on Haloacetic Acids Found as Water Disinfection By-Products, 2018.

[153] W.J. Chen, C.P. Weisel, Halogenated DBP concentrations in a distribution system, J. Am. Water Works Assoc. 90 (1998) 151–163.

[154] A.A. Stevens, L.A. Moore, R.J. Miltner, Formation and Control of Non-Trihalomethane Disinfection By-products, J. Am. Water Works Assoc. 81 (1989) 54–60.

[155] A. Obolensky, P.C. Singer, Development and interpretation of disinfection byproduct formation models using the Information Collection Rule database., Environ. Sci. Technol. 42 (2008) 5654–60.

[156] G.A. Cowman, P.C. Singer, Effect of bromide ion on haloacetic acid speciation resulting from chlorination and chloramination of aquatic humic substances, Environ. Sci. Technol. 30 (1996) 16–24.

[157] C. Shen, P. Norris, O. Williams, S. Hagan, K. Li, Generation of chlorine by-products in simulated wash water, Food Chem. 190 (2016) 97–102.

[158] D.A. Reckhow, P.C. Singer, R.L. Malcolm, Chlorination of humic materials: byproduct formation and chemical interpretations, Environ. Sci. Technol. 24 (1990) 1655–1664.

[159] M.L. Hanson, K.R. Solomon, Haloacetic acids in the aquatic environment. Part II: ecological risk assessment, Environ. Pollut. 130 (2004) 385–401.

[160] V. Kanokkantapong, T.F. Marhaba, B. Panyapinyophol, P. Pavasant, FTIR evaluation of functional groups involved in the formation of haloacetic acids during the chlorination of raw water, J. Hazard. Mater. 136 (2006) 188–196.

[161] T.F. Marhaba, D. Van, The variation of mass and disinfection by-product formation potential of dissolved organic matter fractions along a conventional surface water treatment plant., J. Hazard. Mater. 74 (2000) 133–147.

[162] M. Kitis, T. Karanfil, J.E. Kilduff, A. Wigton, The reactivity of natural organic matter to disinfection by-products formation and its relation to specific ultraviolet absorbance., Water Sci. Technol. 43 (2001) 9–16.

[163] S.A. Parsons, B. Jefferson, E.H. Goslan, P.R. Jarvis, D.A. Fearing, Natural organic matter-the relationship between character and treatability, Water Sci. Technol. Water Supply. 4 (2004) 43–48.

[164] R. Fabris, C.W.K. Chow, M. Drikas, B. Eikebrokk, Comparison of NOM character in selected Australian and Norwegian drinking waters, Water Res. 42 (2008) 4188–4196.

[165] B.S. Karnik, S.H. Davies, M.J. Baumann, S.J. Masten, The effects of combined ozonation and filtration on disinfection by-product formation, Water Res. 39 (2005) 2839–2850.

[166] T. Dittmar, Biogeochemistry of Dissolved Organic Matter, in: Elsevier, Amsterdam, 2015.

[167] F. Meng, G. Huang, X. Yang, Z. Li, J. Li, J. Cao, Z. Wang, L. Sun, Identifying the sources and fate of anthropogenically impacted dissolved organic matter (DOM) in urbanized rivers, Water Res. 47 (2013) 5027–5039.

[168] K. Fukuzaki, I. Imai, K. Fukushima, K.I. Ishii, S. Sawayama, T. Yoshioka, Fluorescent characteristics of dissolved organic matter produced by bloom-forming coastal phytoplankton, J. Plankton Res. 36 (2014) 685–694.

[169] J. Awad, J. van Leeuwen, C. Chow, M. Drikas, R.J. Smernik, D.J. Chittleborough, E. Bestland, Characterization of dissolved organic matter for prediction of trihalomethane formation potential in surface and sub-surface waters, J. Hazard. Mater. 308 (2016) 430–439.

[170] M.H. Chantigny, Dissolved and water-extractable organic matter in soils: a review on the influence of land use and management practices, Geoderma. 113 (2003) 357–380.

[171] R. Haynes, Labile organic matter as an indicator of organic matter quality in arable and pastoral soils in New Zealand, Soil Biol. Biochem. 32 (2000) 211–219.

[172] A.T. Chow, A.T. O’Geen, R.A. Dahlgren, F.J. Díaz, K.-H. Wong, P.-K. Wong, Reactivity of Litter Leachates from California Oak Woodlands in the Formation of Disinfection By-Products, J. Environ. Qual. 40 (2011) 1607.

[173] M.A. Goñi, J.I. Hedges, Lignin dimers: Structures, distribution, and potential geochemical applications, Geochim. Cosmochim. Acta. 56 (1992) 4025–4043.

[174] K.J. Meyers-Schulte, J.I. Hedges, Molecular evidence for a terrestrial component of organic matter dissolved in ocean water, Nature. 321 (1986) 61–63.

[175] S. Opsahl, R. Benner, Distribution and cycling of terrigenous dissolved organic matter in the ocean, Nature. 386 (1997) 480–482.

[176] B. Biddanda, R. Benner, Carbon, nitrogen, and carbohydrate fluxes during the production of particulate and dissolved organic matter by marine phytoplankton, Limnol. Oceanogr. 42 (1997) 506–518.

[177] U. Siegenthaler, J.L. Sarmiento, Atmospheric carbon dioxide and the ocean, Nature. 365 (1993) 119–125.

[178] N. Kawasaki, K. Komatsu, A. Kohzu, N. Tomioka, R. Shinohara, T. Satou, F.N. Watanabe, Y. Tada, K. Hamasaki, M.R.M. Kushairi, A. Imai, Bacterial contribution to dissolved organic matter in eutrophic Lake Kasumigaura, Japan., Appl. Environ. Microbiol. 79 (2013) 7160–8.

[179] K. Kaiser, R. Benner, Major bacterial contribution to the ocean reservoir of detrital organic carbon and nitrogen, Limnol. Oceanogr. 53 (2008) 99–112.

[180] N. Kawasaki, R. Sohrin, H. Ogawa, T. Nagata, R. Benner, Bacterial carbon content and the living and detrital bacterial contributions to suspended particulate organic carbon in the North Pacific Ocean, Aquat. Microb. Ecol. 62 (2011) 165–176.

[181] J.A. Aitkenhead, D. Hope, M.F. Billett, The relationship between dissolved organic carbon in stream water and soil organic carbon pools at different spatial scales, Hydrol. Process. 13 (1999) 1289–1302.

[182] D. Hope, M.F. Billett, M.S. Cresser, A review of the export of carbon in river water: Fluxes and processes, Environ. Pollut. 84 (1994) 301–324.

[183] D.A. Reckhow, P.L.S. Rees, D. Bryan, Watershed sources of disinfection byproduct precursors, Water Sci. Technol. Water Supply. 4 (2004) 61–69.

[184] D.M. Golea, A. Upton, P. Jarvis, G. Moore, S. Sutherland, S.A. Parsons, S.J. Judd, THM and HAA formation from NOM in raw and treated surface waters, Water Res. 112 (2017) 226–235.

[185] E.H. Goslan, Natural Organic Matter Character and Reactivity: Assessing Seasonal Variation in a Moorland Water, (2003).

[186] D. Gang, T.E. Clevenger, S.K. Banerji, Relationship of chlorine decay and THMs formation to NOM size, J. Hazard. Mater. 96 (2003) 1–12.

[187] W. Gan, W. Guo, J. Mo, Y. He, Y. Liu, W. Liu, Y. Liang, X. Yang, The occurrence of disinfection by-products in municipal drinking water in China’s Pearl River Delta and a multipathway cancer risk assessment, Sci. Total Environ. 447 (2013) 108–115.

[188] C. Jung, H. Son, The relationship between disinfection by-products formation and characteristics of natural organic matter in raw water, Korean J. Chem. Eng. 25 (2008) 714–720.

[189] S.W. Krasner, J.P. Croué, J. Buffle, E.M. Perdue, Three approaches for c haracterizing NOM, J. Am. Water Works Assoc. 88 (1996) 66–79.

[190] J.P. Croué, E. Lefebvre, B. Martin, B. Legube, Removal of Dissolved Hydrophobic and Hydrophilic Organic Substances during Coagulation/Flocculation of Surface Waters, Water Sci. Technol. 27 (1993) 143–152.

[191] D.M. Owen, G.L. Amy, Z.K. Chowdhury, Character- ization of Natural Organic Matter and Its Relationship to Treatability, AWWA Research Foundation and American Water, Denver, CO, USA., 1993.

[192] S.K. Golfinopoulos, G.B. Arhonditsis, Multiple regression models: A methodology for evaluating trihalomethane concentrations in drinking water from raw water characteristics, Chemosphere. 47 (2002) 1007–1018.

[193] J.C. Powell, Modelling Chlorine in Water Distribution Networks., University of Birmingham., 1998.

[194] B. Courtis, Water Quality Chlorine Management., he University of Birmingham., 2003.

[195] J. Zhang, J. Yu, W. An, J. Liu, Y. Wang, Y. Chen, J. Tai, M. Yang, Characterization of disinfection byproduct formation potential in 13 source waters in China, J. Environ. Sci. 23 (2011) 183–188.

[196] P. Roccaro, F.G.A. Vagliasindi, Differential vs. absolute UV absorbance approaches in studying NOM reactivity in DBPs formation: Comparison and a pplicability, Water Res. 43 (2009) 744–750.

[197] N. Beauchamp, O. Laflamme, S. Simard, C. Dorea, G. Pelletier, C. Bouchard, M. Rodriguez, Relationships between DBP concentrations and differential UV absorbance in full-scale conditions, Water Res. 131 (2018) 110–121.

[198] R. Sadiq, M.J. Rodriguez, Disinfection by-products (DBPs) in drinking water and predictive models for their occurrence: A review, Sci. Total Environ. 321 (2004) 21–46.

[199] L.C. Hua, J.L. Lin, P.C. Chen, C. Huang, Chemical structures of extra- and intra-cellular algogenic organic matters as precursors to the formation of carbonaceous disinfection byproducts, Chem. Eng. J. 328 (2017) 1022–1030.

[200] J. Wang, Z. Hao, F. Shi, Y. Yin, D. Cao, Z. Yao, J. Liu, Characterization of Brominated Disinfection Byproducts Formed during the Chlorination of Aquaculture Seawater, Environ. Sci. Technol. 52 (2018) 5662–5670.

CHAPTER 3

MATERIALS AND METHODOLOGY

Chapter 3

Materials and Methodology

3.1 Study Area and sampling

Seawater samples were collected monthly once from the intake Jetty, outfall discharge and mixing point of Madras Atomic Power Station (MAPS), Kalpakkam (12º33´N; 80º11´E) located on the Bay of Bengal coast, India (**Figure 3. 1**). The outfall discharge of MAPS has four bays, two for process cooling seawater-I and II (PSW-I and PSW II), and two for condenser cooling seawater-I and II (CSW-I and II). Samples from each bay were collected at the outfall of MAPS. The discharge seawater travels through an artificial canal of about 800 m before meeting the sea at mixing point. MAPS consist of two pressurized heavy water reactors (235 MWe each) and uses approximately 30 m^3 s^{-1} seawater for condenser cooling in the once-through cooling system. Seawater drawn for MAPS condenser cooling is chlorinated at the intake point, and the treated water is discharged back to sea through an 800 m long canal. Seawater is drawn by gravity through a submarine tunnel of 468 m long and 3.8 m diameter, built 53 m below the seabed. The intake system is such that it takes approximately 5–7 min for the seawater to travel from the intake to the discharge outfall when both the reactors are operating. Chlorine residual and DBPs concentrations were monitored in the discharge water, and disinfection experiments were carried out for the water samples collected at MAPS jetty. Water samples from Palar sub-soil and open reservoir were collected monthly in duplicate to investigate the DBPs formation potential in relation to change in various physicochemical parameters. Further representative seawater (SWR), Palar river water (RVR) and reservoir water (RSR) samples were collected periodically and whenever required for experimental studies. The Palar River located in the district of Kancheepuram, Tamil Nadu, India, is the main source for the drinking water supply to the neighborhood. Water samples from a covered, concrete-lined infiltration well located inside the Palar river bed are transported to the open reservoir 20 km away from the river bed, located at Kalpakkam (**Figure 3. 2**). The reservoir receives water from the Palar riverbed infiltration well through a 60 cm diameter cast iron pipe. It has a storage capacity of 30,000 m^3, with a spread over an area of about 2 ha and has a maximum depth of 3 m. Other than rainwater, there is no external linkage to this reservoir. The reservoir caters for the freshwater need of various laboratories of the Indira Gandhi Centre for Atomic Research (IGCAR) as well as the demineralization plants of both the Madras Atomic Power Station (MAPS) and the Fast Breeder Test Reactor (FBTR). Moreover, it also serves as a drinking water source to IGCAR and MAPS.

Two liters of water samples from each of the locations were collected in a pre-cleaned, air-tight high-density polyethylene (HDPE) bottle during each sampling and were brought to the laboratory within 30 min. Samples were filtered immediately after reaching the laboratory through a Millipore 0.45 µm nylon membrane filter. Filtered samples were kept separately in 1 L polytetrafluoroethylene (PTFE)-lined screw cap glass bottles for chlorination experiments. All samples were stored in the dark at 4^0C until the analysis of physicochemical parameters of water and all the analyses/experiments were completed within three days of sample collection.

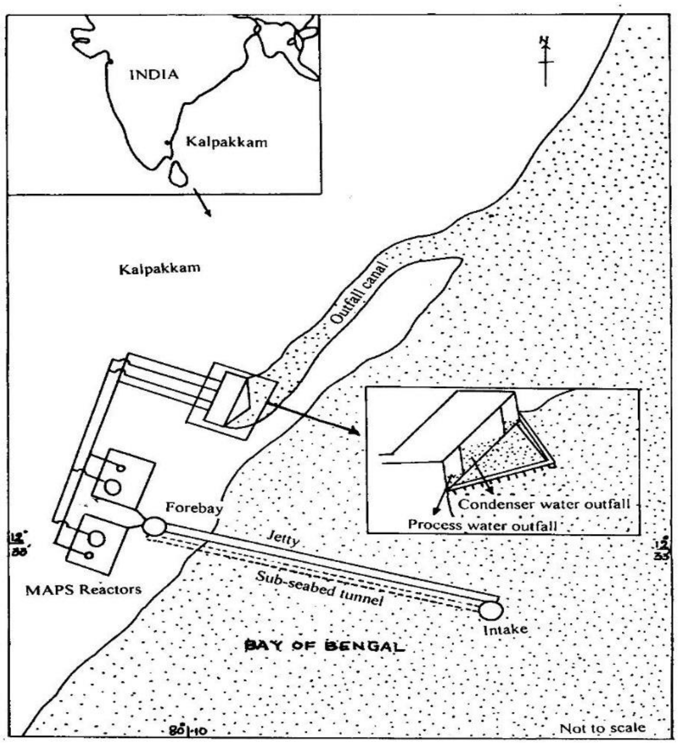


Figure 3.1 Schematic of cooling seawater system of Madras Atomic Power Station (MAPS) showing the intake point, intake tunnel, outfall, discharge canal, and mixing point.

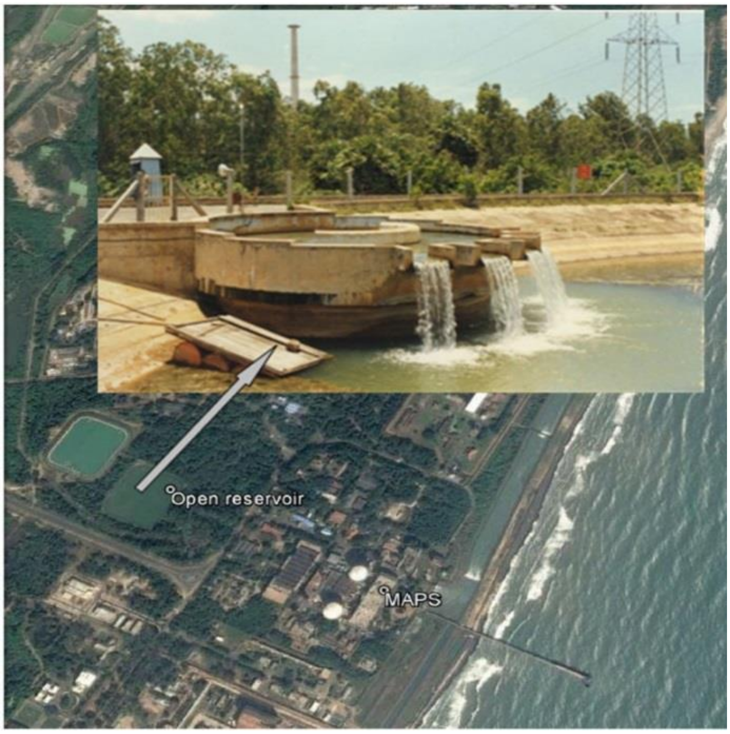


Figure 3. 2 Actual photograph of the open reservoir receiving the Palar River water

3.2 Materials

3.2.1 Reagents

Certified reference material of THMs calibration mix (100 μg/mL each in methanol) and EPA 552.2 HAAs mix containing 2000 μg/mL of each component were obtained from SUPLECO, USA. Solvents (methyl tert-butyl ether (MTBE), Pentane, Methanol, Acetone) are HPLC grade purchased from Sigma-Aldrich chemicals. NaOCl stock solution (~4%) used was obtained from EMPLURA Merck, India. Chemicals Na_2SO_4 (GR, 99.5%), $Na_2S_2O_3$ (GR, 99.5%), $NaHCO_3$ (ACS, ISO 99.9%), Na_2CO_3 (ACS, ISO 99.9%), H_2SO_4 (ACS, 98%), HNO_3 (Ultrapure 65%) were procured from Merck Germany. Bromide, chlorate, and chlorite IC standards were procured from Sigma Aldrich chemicals, and $NaClO_2$ (min assay 80%) was obtained from HIMEDIA, India.

3.2.2 Chlorine stock solution

Chlorine stock solution was prepared by diluting 5 mL of concentrated 4% sodium hypochlorite in a 250 mL volumetric flask with Milli-Q water, and the concentration was between 1200 to 1400 mg/L Cl_2. The solution was then stored in an amber color bottle at 4 °C. The stock solution was diluted appropriately to prepare the working solution and standardized by Iodometric titration before the start of each set chlorination experiments.

3.2.3 Chlorine Dioxide stock solution

Since chlorine dioxide gas is explosive and tends to decompose upon heating, it is not suitable for storage and transport. Hence it is usually produced immediately before use. Chlorine dioxide was produced with a laboratory scale generator by acid activation of sodium chlorite. The experimental setup for the generation of chlorine dioxide in the laboratory is shown in **Figure 3. 3**. The stoichiometry of the reaction is as follows.

$4NaClO_2 + 2H_2SO_4 \rightarrow 2ClO_2\uparrow + 2Na_2SO_4 + HCl + HClO_3 + H_2O$

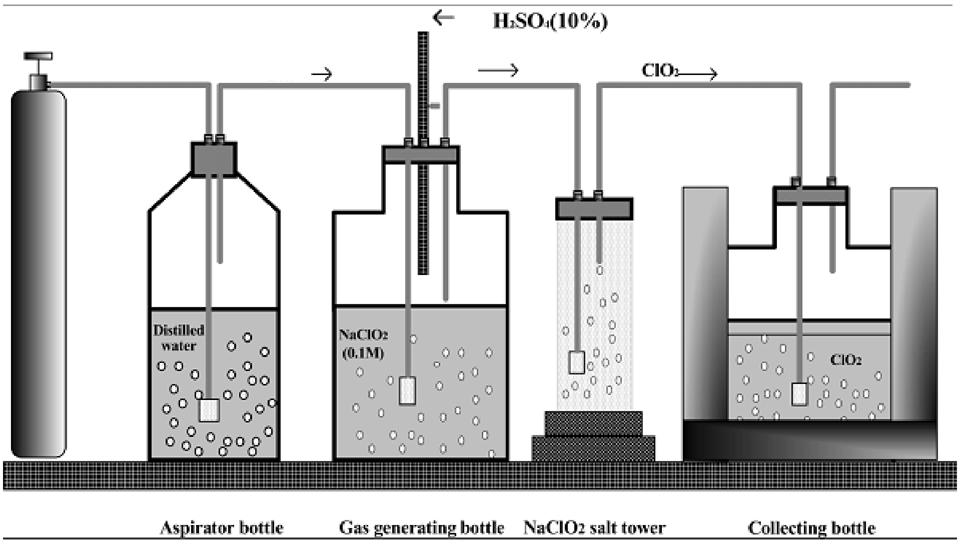


Figure 3. 3 Schematic of chlorine dioxide generation by the acid activation of $NaClO_2$

The reaction flask and gas scrubbing salt tower were filled with 500 mL 0.1M $NaClO_2$ solutions. 50 mL of sulphuric acid solution was added drop by drop to the reaction flask. The ClO_2 gas generated was purged by bubbling nitrogen gas through the solution. N_2 gas flow was maintained for 30 mins after the completion of H_2SO_4 acid addition. The chlorine dioxide gas driven off by sparging with nitrogen gas was carried through three traps kept in series as shown in **Figure 3. 3** and finally absorbed into the ice-cold distilled water. The concentration of ClO_2 aqueous solution generated by this way was 1000-2000 mg/L. At STP, the solubility of chlorine dioxide in water is 3.0 g/L and decreases with increase in temperature. The chlorine dioxide solutions were standardized by Iodometric titration method, and its concentration was determined at the beginning of each experiment. Chlorine dioxide solutions were kept in an airtight amber color bottle at 4^0C while not in use to avoid its decomposition.

3.3 Methodology

3.3.1 Experimental methods

3.3.1.1 Chlorine and chlorine dioxide treatment

Chlorine and chlorine dioxide treatment of raw water samples, as well as aqueous extracts of isolated organic fractions from algae, bacteria and soil, were carried out in 500 ml amber color glass bottle. Palar and Open reservoir samples were buffered to pH 7.5 with 5 mM phosphate buffer, and seawater samples were used as such. Water samples were treated with a calculated amount of Cl_2 or ClO_2 working standard for the desired oxidant dose. Residual oxidant concentration at various intervals was measured by the DPD-colorimetric method. A portion of treated samples was withdrawn at different time intervals for further extraction and analysis of THMs and HAAs.

To study the effect of chlorine and chlorine dioxide dose on the kinetics of THM and HAAs formation, various Cl_2 and ClO_2 doses such as 1, 3, 5, 10 and 25 mg/L were reacted with at various temperatures such as 20, 30, and 40^0C. Samples were analyzed for the concentration of CBPs at different reaction time ranging from 5 min to 168 h for the (Note: experimental conditions in each chapter may be different to elucidate the set objectives and would be indicated in the respective chapter). Before the start of the experiments, samples were incubated for about 2 h at constant experimental temperatures to equilibrate the samples. Subsequently, samples were treated with calculated amount of standardized chlorine and chlorine dioxide solution, and the temperatures were maintained constant throughout the experiments. At the desired time intervals, 5 mL and 90 mL each of the treated samples were withdrawn separately for THMs and HAAs analysis respectively. Residual Cl_2 and ClO_2 present were quenched by immediate addition of stoichiometrically excess amount of sodium thiosulphate ($Na_2S_2O_3$) to stop further reactions. Samples were also withdrawn at the same time intervals for determination of the available Cl_2 and ClO_2 residual.

To investigate the THMs and HAAs formation potential of various NOM sources namely algal, bacterial and soil, corresponding aqueous extracts were buffered to pH 7 and treated with different concentration of Cl_2 and ClO_2. In the case of algae and bacteria, NOMs were isolated into extracellular and intracellular organic matter which were again fractionated to hydrophobic, transphilic and hydrophilic fractions. Whereas, in the case of soil, the organic content was separated as acid leachable and alkali leachable organics which were further fractionated to hydrophobic, transphilic and hydrophilic fractions. All the aqueous organic extracts were reacted with Cl_2 and ClO_2 to evaluate reactivity and DBP formation potential. Samples were withdrawn from the reaction vessel at the desired time intervals for different Cl_2 and ClO_2 dose for measurement of residual oxidant as well as for the analysis of THMs and HAAs.

3.3.1.2 Isolation of NOM from different sources

Organic matter was isolated from a blue-green algae *Spirulina Platensis* monoculture solution and bacterial mixed culture as aquagenic sources of natural organic matter to the aquatic ecosystem. As pedogenic source, a number of soil samples collected around the landscape near the studied water sources and were pooled together to obtain a composite soil sample. Algal and bacterial organic content were separated as extracellular and intracellular organic matter (EOC and IOC). The soil sample was treated with alkali and acid sequentially get the base and acid leachable soil organic content (SOCA and SOCB). All the above isolated organic contents were further fractionated into hydrophobic (HPO), transphilic (TPI) and hydrophilic components as per the procedure described below.

3.3.1.3 Algae culture

Spirulina platensis is an alkaliphile that thrives in alkaline marine environments at pH 11 and above. They are native colonizers of tropical and subtropical water bodies. *Spirulina platensis* used in the study was grown in Zarrouk's medium [1] maintained at pH 10. *Spirulina platensis* was obtained from the germplasm collections of National Facility for Marine Cyanobacteria (NFMC), Trichy and the axenic culture was being maintained in the laboratory conditions for future experiments. Under aseptic conditions, 150 mL of sterile medium was taken in a 250 mL Erlenmeyer flask and was inoculated with 15 mL mid-log phase culture of *Spirulina platensis*. The culture was incubated at 25±2°C under white fluorescent light at an intensity of 60 µmol photon m^{-2} s^{-1}, measured by a standard photometer. The culture flasks were exposed to a day-night cycle of light (16 h light: 8h dark) for better and rapid growth and harvested in the mid-exponential growth phase. The culture flasks were kept in continuous shaking at 120 rpm, and growth was monitored by its absorbance at 684 nm with a spectrophotometer. The cell density of the algal suspension was adjusted to 1.0 x 10^6 cells/L by diluting with the original medium and used for further experiments.

3.3.1.4 Extraction of EOC and IOC from algal suspension

The procedure followed for the separation of EOC and IOC from algal suspension was similar to that described by Pivokonsky et al. (2014) [2]. To extract the EOM and cells, the harvested algae suspension was transferred to several 50 mL tubes and then centrifuged at ~3000 g for 20 min at 25^0C in a 6 X 50 mL rotor (Remi R-24, India). Supernatants from all the centrifuge tubes were slowly transferred to a 1 L beaker, the EOC obtained was filtered through 0.45 µm Whatman filter and designated as raw algal-EOC (AEOC). The algal cells residue remained in the centrifuge tubes and on the filter-papers were collected and re-suspended in a simulated aqueous solution composed of 0.5 mM $CaCl_2$, 1.0 mM $NaHCO_3$, and 15.0 mM $NaClO_4$ in Milli-Q water. To extract IOC by cell lysis, the algal residue was subjected to three freeze thawing-sonication cycle, which was a successive process of freezing at −20 °C for 8 h followed by thawing at 30 °C for 2 h and sonication for 15 min. The Finally, IOC released into the aqueous solution was separated by centrifugation and microfiltration same as above. The filtrate was referred to as algal-IOC (AIOC). The schematic of experimental procedures for EOC and IOC separation is shown in **Figure 3. 4**.

3.3.1.5 Bacterial culture

Titanium panels (12 X 9 X 0.3 cm^3) were immersed in the coastal water at a depth of 1 m for 48 h, at MAPS jetty. The biofilm containing bacterial colony was scrapped out and inoculated with 500 ml of sterilized Zobell marine broth. The culture was incubated for 72 h to obtain an amplified dense bacterial suspension. OD_{600} was measured and compared with Mcfarland standard 4.0 with appropriate dilution for cell density determination. The bacterial suspension was centrifuged in a number of 50 mL centrifuge tube and extracted to 500 ml glass bottle with 0.9% NaCl solution.

3.3.1.6 Separation of EOC and IOC from bacterial culture

EOC and IOC of the bacterial culture were isolated following the procedure described in earlier studies [3,4]. The schematic of the isolation procedure is depicted in **Figure 3. 5**. For EOC extraction, the supernatant centrifugate was mixed with ethanol in 1:2 ratio and was kept at -20^{0}C for overnight for the precipitation of EOC. The resulting solution was centrifuged, and the residue was filtered through a 0.45 μm Whatman filter, washed three times with Milli Q water and resolubilized in water. The resultant aqueous solution was designated as bacterial-EOC (BEOC). The bacteria cells were resuspended in milli-Q water and subjected to three freezing-thawing-sonication cycles similar to AIOC extraction. Finally, the resulting solution was centrifuged, and the centrifugate was filtered using 0.45 μm Whatman filter and designated as bacterial-IOC (BIOC).

3.3.1.7 Extraction of Organic matter from soil

Traditional method of acid and alkali leaching method was adopted for extraction of soil organic content [5,6]. Briefly, 10 gm of dried, ground to 63 μm and homogenized soil sample was treated with 500 mL of 1N NaOH in a polyethylene flask. It was kept on an ultrasonic shaking bath (Sonic-420, Korea) at room temperature for 1 h. The dark-colored extract was separated from insoluble residues by centrifugation was regarded as base leachable dissolved organics present in the soil (SOCB). The remaining residue was extracted with 500 mL 1N HCl following ultrasonication for 1 h. The suspension was centrifuged and filtered through a 0.45 μm filter paper and treated as acid leachable soil organic content (SOCA). Both SOCA and SOCB fractions were adjusted to pH 7 and total organic carbon was analyzed. The schematic of SOCA and SOCB isolation is presented in **Figure 3. 6.**

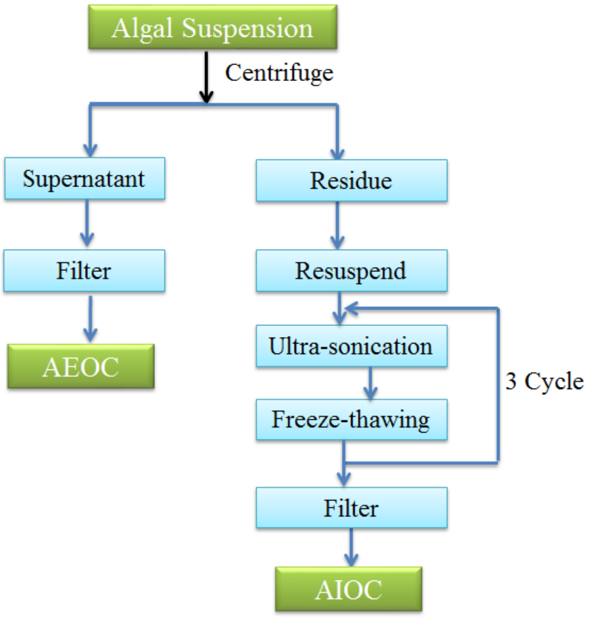


Figure 3. 4 Schematic of experimental procedures for algal extracellular and intracellular organic content (AEOC and AIOC).

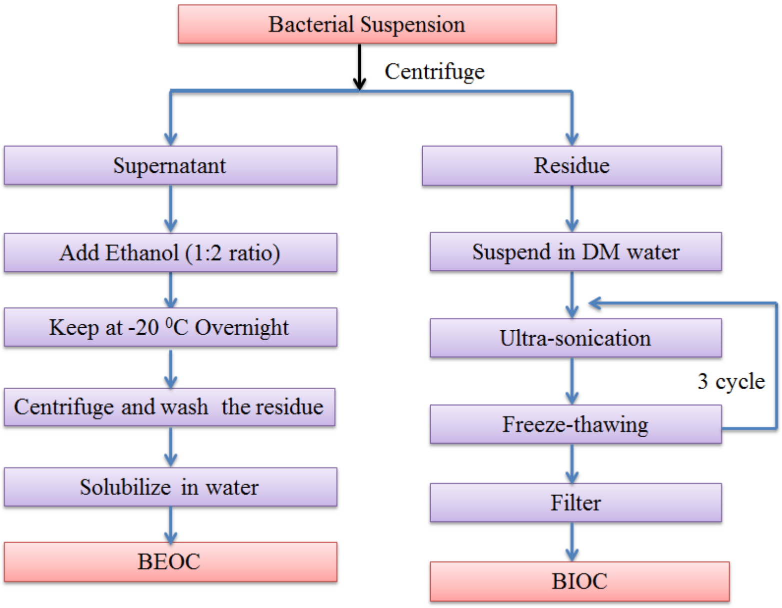


Figure 3. 5 Schematic of the isolation procedure for bacterial EOC and IOC (BIOC and BEOC)

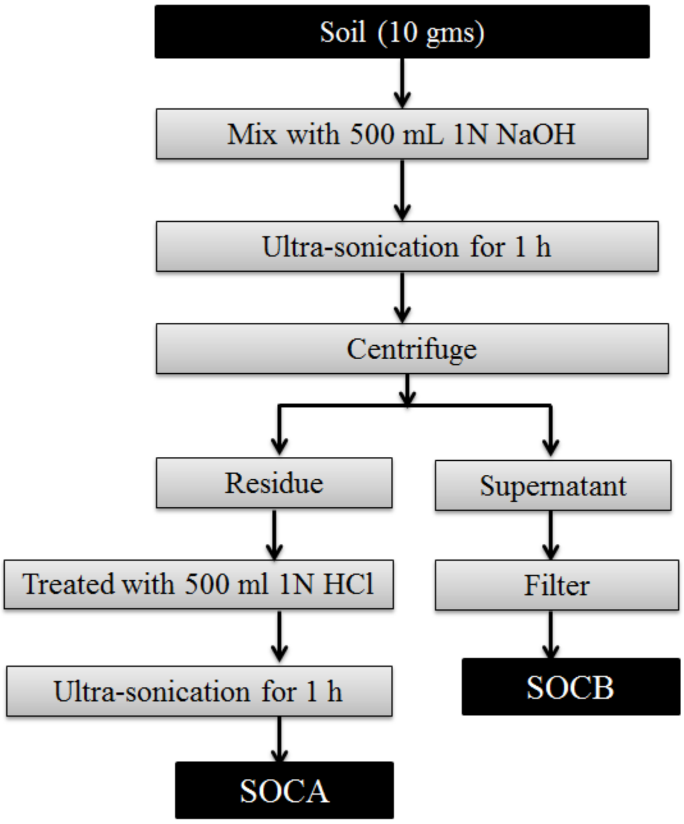


Figure 3. 6 Schematic of separation of alkali (base) leachable and acid leachable organic content (SOCA and SOCB)

3.3.1.8 Fractionation of NOMs

The method described by Malcolm and MacCarthy (1992) was used for the fractionation of AIOC, AEOC, BIOC, BEOC, SOCA, and SOCB into their respective hydrophilic (HPI), hydrophobic (HPO) and transphilic (TPI) constituents. 250 mL each of the above extracts were adjusted to pH 2 (with 2 M HCl). The acidified solutions were consecutively passed through the two columns of 1.5 cm diameter and 100 mm length, connected in a series and filled with 50 mL of XAD-8 and XAD-4 resin, respectively (**Figure 3.7**). The HPO fraction was retained by DAX-8 resin, the TPI fraction was that which passed through XAD-8 but retained by XAD-4 resin, and the fraction passed through both XAD-8 and XAD-4 represented the HPI fraction. Adsorbed HPO and TPI fractions were eluted from the resins with 150 mL of 0.1 M

NaOH with an elution flow rate of 1 mL/min. TOC concentrations of each fraction were determined.

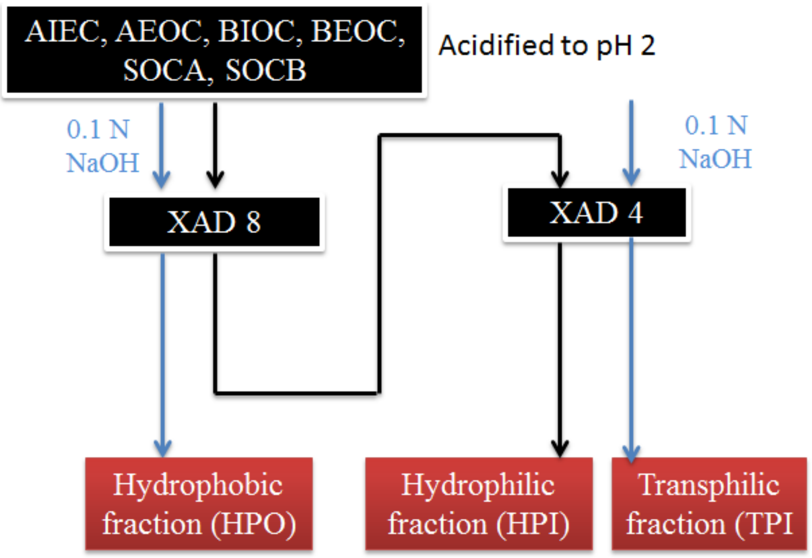


Figure 3. 7 Fractionation of organic content in the aqueous samples based on XAD-8 and XAD-4 resin adsorption

3.3.2 Analytical methods

3.3.2.1 Chlorine and chlorine dioxide analysis

Chlorine and chlorine dioxide stock (~1000-2000 mg/L) and working standard (50-200 mg/L) solutions were prepared as per the procedure described already and standardized by iodometric titration [7]. It is extremely important that, ClO_2 solutions used for the study to be devoid of chlorine for correct comparison of THMs and HAAs formation during both the biocides treatment conditions. The concentration of the ClO_2 stock solution was determined by the iodometric titration similar to chlorine analysis. Cl_2 and ClO_2 residual in the treated experimental solutions were analyzed by DPD colorimetry [8].

Iodometry

In iodometric method, the oxidant analytes oxidize iodide ion to iodine; the liberated iodine is titrated against standard sodium thiosulfate ($Na_2S_2O_3$) solution. The titrations were performed manually by using starch-iodide indicator (accuracy ± 0.18 mg/L). The reactions involved are shown in eqs 2.1-2.3.

$$\mathrm{HOCl} + 2\mathrm{I}^- + \mathrm{H}^+ \rightarrow \mathrm{I}_2 + \mathrm{Cl}^- + \mathrm{H}_2\mathrm{O} \qquad (2.1)$$

$$2\mathrm{ClO}_2 + 2\mathrm{I}^- \rightarrow \mathrm{I}_2 + \mathrm{ClO}_2^- \qquad (2.2)$$

The liberated iodine was then titrated against a standard solution of sodium thiosulphate using a freshly prepared starch solution as an indicator. The chemical reactions involved can be given as follows.

$$2\mathrm{Na}_2\mathrm{S}_2\mathrm{O}_3 + \mathrm{I}_2\ (\text{blue color}) \rightarrow \mathrm{Na}_2\mathrm{S}_4\mathrm{O}_6 + 2\mathrm{NaI}(\text{colorless}) \qquad (2.3)$$

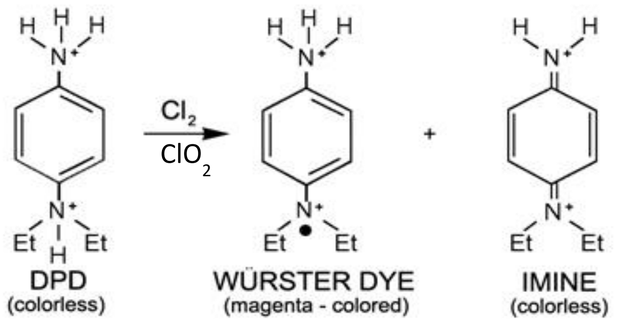
The iodometric titration method was used for concentrations of ClO_2 > 200 mg/L. The oxidation of the iodide by ClO_2 takes place at neutral pH (pH=7) and leads to the release of one mole of iodine (I_2) for every two moles of ClO_2. ClO_2^-, on the contrary, do not react with iodide in neutral pH, however, at pH 2 the reaction proceeds further as per the below equation and complete with reduction of ClO_2 to Cl^- (eq 2.4).

$$ClO_2^- + 8H^+ + 8I^- \rightarrow 2I_2 + Cl^- + 4H_2O \qquad (2.4)$$

The iodine which is formed in neutral solutions ($ClO_2 + e^- = ClO_2^-$) is in a ratio of 1/5 compared with the titration carried out at pH 2.

DPD colorimetry

Residual oxidants of low concentrations (< 10 mg/L) were measured using DPD (N, N-diethyl-p- phenylenediamine) colorimetry using portable colorimeter as per the instrument protocol (Lovibond, MD-200,). In this method, DPD tablet was added to the sample in a 10 mL vial. The DPD get oxidized by the chlorine and chlorine dioxide residual present in the sample to produce a magenta colored compound known as Wurster Dye, and a colorless imine is also forms as a minor product (eq. 2.6). The color imparted by the Wurster dye was measured photometrically at 530 nm using a colorimeter. Even though the photometer system was calibrated by the manufacturer, calibration was verified by spiking the Millipore water with a known concentration of standards before each set of experiments. In the case of the measurement of chlorine dioxide, the absence of chlorine was confirmed by measuring the concentration in the presence and absence of glycine [9]. DPD-1 tablet was used for the determination of free residual chlorine (FRC), and total residual chlorine (TRC) was measured by adding a DPD-3 tablet to the same test solution, combined residual chlorine was calculated as subtraction of TRC and FRC. In the case where only TRC was to be measured DPD-4 tablet was used [10].



(eq. 2.6)

3.3.2.2 THMs Analysis

A mixture of four THM standards was purchased from Sigma Aldrich. Working standards of THMs mix for calibration were prepared by spiking into deionized water to get a series of concentration varied from 0.1 to 100 µg/L of individual THMs species. USEPA method 551.1 for the liquid-liquid extraction and gas chromatography-electron capture (GC-ECD) measurement was employed with minor modifications to extract and quantify THMs. Screw cap glass vials (10 mL) were used for the liquid-liquid extraction. Water samples (5 mL) were transferred to the glass extraction vials using an autopipette. To each 5 mL of water sample in the extraction vial, 2 mL of pentane, was added gently. Then 2 g of reagent grade sodium sulfate (Na_2SO_4) was added to the extraction vial to enhance the partitioning of the THMs into the organic phase and also to minimize the solubility of pentane in water samples. Extraction vials were closed tightly, laid horizontally on a shaker platform, and shaken at 300 rpm for 15 min. After shaking, the vials were allowed to settle for at least 10 min, and 2 mL of the upper layer of pentane was transferred using an airtight glass syringe into a 2 mL GC vials for subsequent analyses. Analysis of THMs was carried out with a gas chromatograph attached with an electron capture detector (ECD) attached with an autosampler (GC-1110, Thermo Scientific, India), the ECD detector is highly sensitive to haloorganics. Identification of the four THMs species was confirmed by injecting individual THM standards and identified by the retention time. Quantification of the THMs species was carried out by external standard calibration, and Iris software was used for chromatogram peak integration. The capillary GC column CB-5 column with ID, 0.25 mm, film thickness, 0.25 μm and length, 30 m (Cyber Lab, USA) was used both in GC-MS/MS and GC-ECD with same operating conditions. For the separation of four THMs species, the injection and detector temperatures were maintained at 150°C, and 260 °C, and oven temperature program was set as follows: 30 °C-10 min - @3^0C/min - 41 °C – 6 min - @ 5^0C/min - 81°C – 0 min - @ 25^0C/min – 180°C 6 min. **Figure 3. 8** shows an overlaid chromatogram of various samples and standards analyzed by GC-ECD. The injection was set as split mode with split ratio 1:5 with an injection of 2 μL of pentane extract.

Ultra-high pure (99.999%) nitrogen gas was used both as a carrier and makeup gas for GC-ECD, whereas ultrapure helium gas was used as GC-MS carrier gas. A minor change in the retention time and detector response is expected over a period of time for GC analysis, and relevant details would be mentioned in the respective chapter.

3.3.2.3 HAAs Analyses

A mixture of nine HAAs standards was purchased from Sigma Aldrich. The preparation of HAAs calibration standards was similar to that of THMs. USEPA method 552.2 with some modifications was employed for the liquid-liquid extraction, analysis, and quantification. This method is based on the acid catalyzed esterification of the HAAs before analysis by GC. Briefly, to the 90 mL of water sample in a glass extraction vial, 2 mL of concentrated (98%) H_2SO_4 was added to the water to convert the acetates to their corresponding acids. HAAs was extracted from the aqueous solution with 5 mL of methyl - tertiary butyl ether (MTBE) by shaking vigorously for 15 min at 300 rpm in a mechanical shaker. Prior to MTBE addition, about 16 g anhydrous sodium sulfate was added to the extraction vial to enhance the partitioning of the HAAs into the organic phase and also to minimize the MTBE water solubility. The extraction vials were allowed to settle for at least 10 min to separate the two phases. After settling, 3 mL of the upper MTBE layer was transferred to a 10 mL glass vial for the derivatization of HAAs to their corresponding esters. For the esterification, 1mL of 10% acidified methanol was added to the MTBE extract and allowed to react for 2 hours at 50^0C in a water bath for the complete conversion of HAAs to their corresponding methyl esters. The resultant reaction mixture was treated with 6 mL of 15% anhydrous sodium sulfate solution, and the upper organic layer was transformed to a vial containing 4 mL of saturated sodium bicarbonate solution to neutralize the solution. Finally, 2 mL of the organic upper layer was transferred to a GC vial for analysis. The same GC-MS/MS, GC- ECD and GC column that was used for THMs analysis were used for identification and regular analysis of HAAs as well. The GC oven temperature program followed was, initial oven temperature: 35°C, hold time 15 mins, 5°C/min up to 75°C held for 10 mins, 5°C/min up to 100 °C, and held for 5 min, and 5 °C/min up to 135°C held for 2 mins, and 25^0C/min up to 200^0C and held for 0 min. Total run time was 57 mins. Injection and detector temperature were maintained at 150°C and 260°C respectively. **Figure 3. 9** and **Figure 3. 10** depicts the GC-MS and GC-ECD chromatogram respectively for the HAAs analysis.

3.3.2.4 pH, Temperature, Conductivity & Dissolved Oxygen

pH, temperature, conductivity and dissolved oxygen (DO) of the water samples were measured using a portable multiparameter probe (HI 9829, Hanna Instruments, USA). The instrument was calibrated for pH and conductivity using a standard buffer and KCl standards respectively before sampling. DO sensor was calibrated with calibration-0 (oxygen-free water) and calibration-100 (air saturated water) water. Cal 0 was prepared by adding 1g Na_2SO_3 and 50 µL of 1000 mg/L $Co(NO_3)_2$ to 1000 mL of Millipore water as per the instrument manual. Cal 100 was prepared by saturating the water with oxygen by blowing air into the water continuously for 2 min.

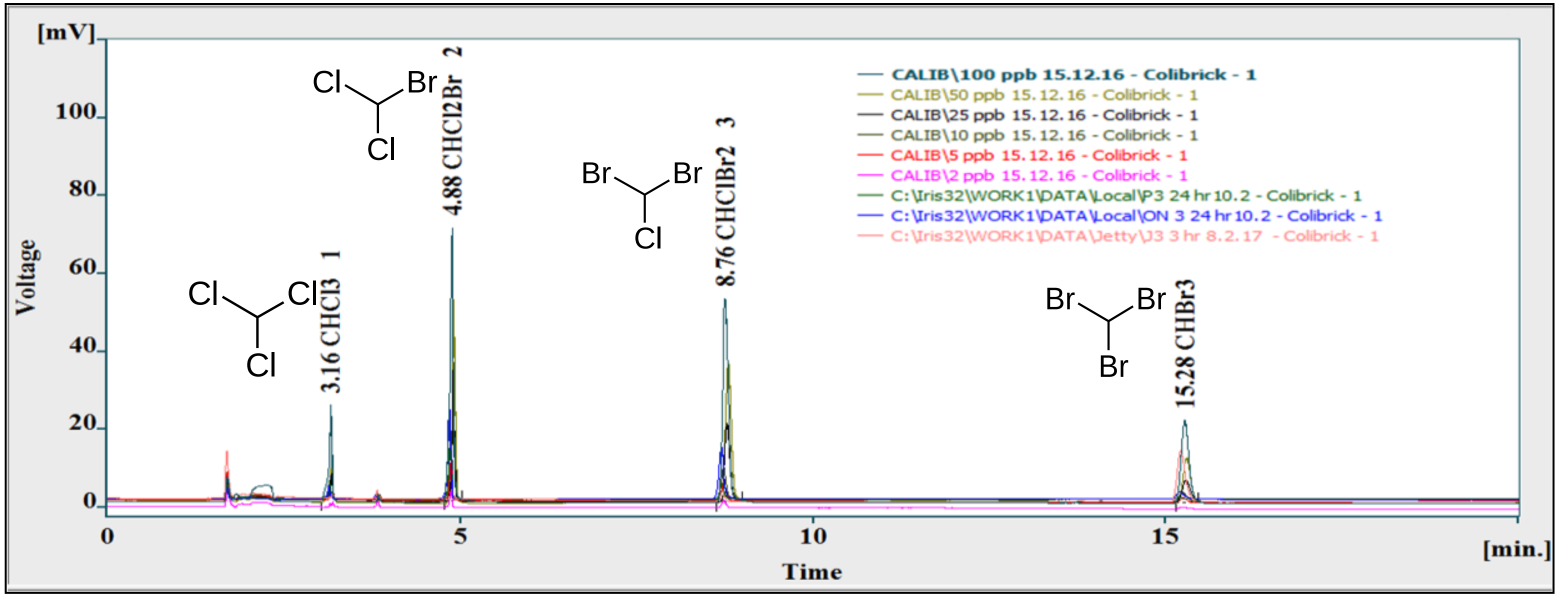


Figure 3. 8 Overlaid chromatogram of THMs obtained for various samples and standards analyzed by GC-ECD

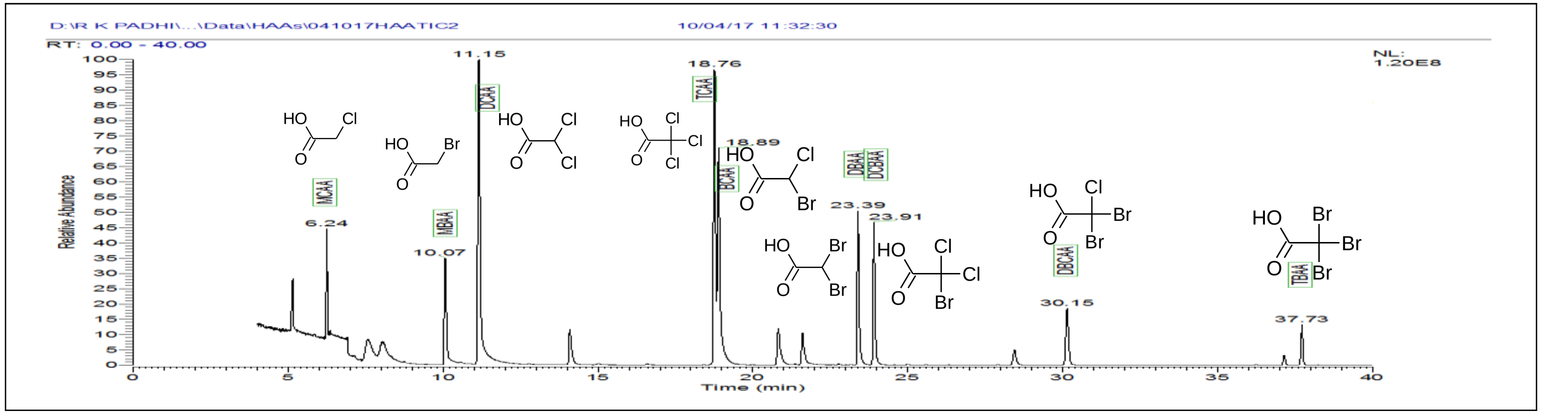


Figure 3. 9 GC-MS total ion chromatogram for the identification of HAAs species

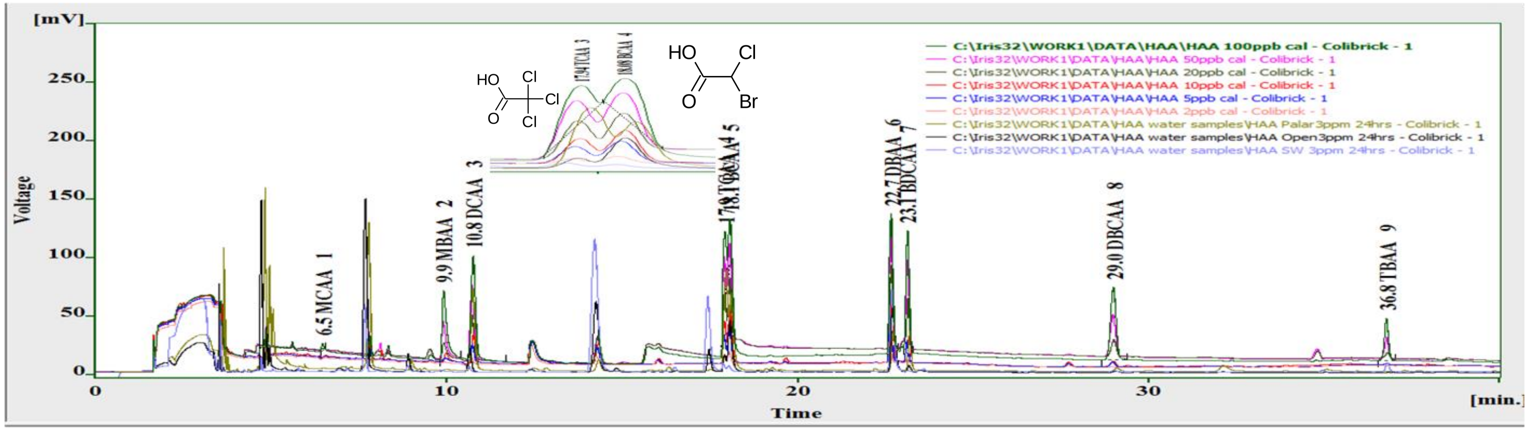


Figure 3. 10 GC-ECD chromatogram of HAAs analyzed for standards and samples

3.3.2.8 Dissolved Organic Carbon

Dissolved organic carbon (TOC) was measured using TOC analyzer (TOC-VCSH Analyzer, Shimazdu, Japan) based on the principle of high-temperature combustion oxidation and near infrared detection. Samples for TOC analysis was preserved at 4°C in the refrigerator and analysis were completed within two days of collection. Prior to TOC analysis, inorganic carbon present in the samples was purged out by the analyzer with automatic addition of phosphoric acid. TOC standards were prepared from 1000 mg C/L stock solutions of potassium hydrogen phthalate, and calibration curves were generated for the TOC concentrations ranging from 0.2-15 mg C/L. Samples with TOC concentration above the calibration range were diluted appropriately and measured again.

3.3.2.9 Nitrate, Nitrite and Total Nitrogen

Water quality descriptors such as NO_3^-, NO_2^- and total nitrogen (TN) were measured using a nutrient auto analyzer (SAN$_{++}$ 126 System, SCALAR, Netherland). The automated determination for the determination of nitrate and nitrite is based on the conventional cadmium reduction-UV determination method. The sample was buffered to pH 8.2 and passed through a column containing granulated copper-cadmium to reduce NO_3^- to NO_2^-. The nitrite originally present plus reduced nitrate is determined by diazotizing with sulfanilamide and coupling with N-(1 naphthyl) ethylenediamine dihydrochloride to form a highly colored azo dye which was measured at 540 nm by the UV detector. Nitrite content in the sample was directly measured without subjecting to Cd column. TN was determined similar to nitrite after oxidizing all the nitrogen species present in the sample to nitrate by per-sulphate oxidation followed by reduction to nitrite. Nitrate, nitrite, and total nitrogen (TN) calibration standards were prepared from 1000 mg N/L stock solution of sodium nitrate for the quantification.

3.3.2.10 UVA_{254} and $SUVA_{254}$

UVA_{254} was determined using double beam spectrophotometer (Spectrascan UV132 VIS 2600, Thermo Fisher Scientific, USA). Samples were placed in a quartz cuvette of 10 mm pathlength and measured at a wavelength of 254 nm. The spectrophotometer was zeroed by measuring the absorbance of Millipore water after several rinses. The instrument was zeroed after every ten samples, and method performance was monitored using total organic carbon standards made with potassium hydrogen phthalate. Specific UV Absorbance (SUVA) was also calculated by normalizing UVA_{254} by DOC content. $\mathrm{SUVA}_{254} = \frac{\mathrm{UV}_{254}*100}{\mathrm{DOC\ in\ mg/L}}\ (\mathrm{L\ mg\text{-}C^{-1}\ m^{-1}})$

3.3.2.11 Bromide

Bromide was measured as per USEPA method 300.1 [11] using an ion chromatography system coupled with a conductivity detector (940 Professional IC Vario, Metrohm, Switzerland). Separation of Br^- and other interfering anions were carried out with a Metrosep A Supp 5-250/4.0 anion column coupled with a Metrosep A SUPP 5 Guard /4.0 guard column (Chromatogram is shown in **Figure 3. 11**). The eluent used was 3.2 mM Na_2CO_3/1 mM $NaHCO_3$ with a flow rate of 1 mL per min. Calibration curves were obtained by a series of standard concentrations ranging from 5 to 400 µg/L which was prepared from mixed anions IC standards (99.9% minimum, from Sigma-Aldrich). Bromide content in freshwater samples was determined directly. However, seawater samples were diluted 25 times before analysis to avoid salt loading to the IC columns. The limit of detection of bromide was 0.01 mg/L

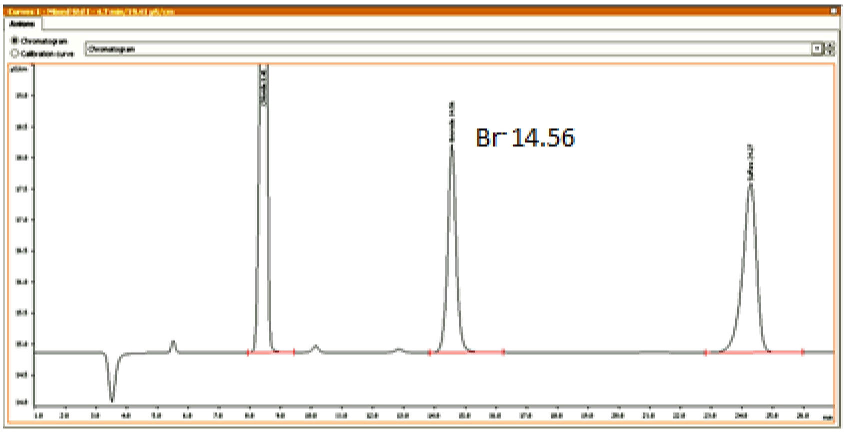


Figure 3. 11 Ion chromatogram showing separation of bromide from the interfering anions

3.3.2.12 Chlorate and chlorite

Concentrations of chlorite and chlorate in the samples were determined by ion chromatography as per the method USEPA method 300.1[11] (Chromatogram as shown in **Figure 3. 12)**. Thermo Scientific Dionex Ion chromatograph, ICS-2500 was used with Ion pack AS 19 analytical columns coupled with AG 19 guard column for the chlorate chlorite determination. For ClO_2 treated samples, residual ClO_2 was removed by purging with nitrogen to avoid interference with the analysis. The standard solutions of chlorite and chlorate were prepared by dilution of the 1000 mg/L IC standards. The limits of detection were 0.010 mg/L for chlorite and 0.012 mg/L for chlorate.

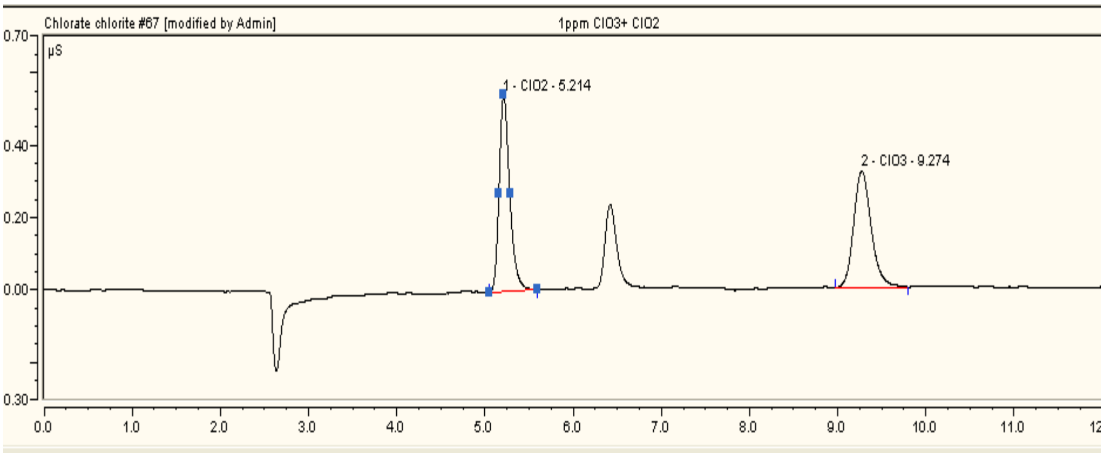


Figure 3. 12 Ion chromatogram for the Chlorate and chlorite analysis

3.3.2.13 Chlorophyll-a

Chlorophyll-a (Chl-a) was determined using double beam spectrophotometer (Spectrascan VIS 2600, Thermo Fisher Scientific, USA) following the method of Parson et al. (1984) [12]. Samples were filtered immediately within one hour of collection. The filter paper was carefully removed from the holder. Pigment extraction was carried out by extracting with 90% acetone and was made up to the required volume. The absorbance of the sample extract was measured at 750, 664, 647 and 630 nm, referenced against 90% acetone as blank. Concentrations of Chl-a was calculated as

Chlorophyll-a = $(11.85*(E_{664} - E_{750}) - 1.54* (E_{647} - E_{750}) - 0.08 (E_{630} - E_{750})) * Ve/L*Vf$; where, L = Path length (in cm) Ve = Extraction volume in mL, Vf = Filtered volume in L.

References

[1] C. Zarrouks, “Contribution a Letude and Une cyanophycae. Influence de divers factors physiques et chimiques sur La Croissance et la Photosynthesis de Spirulina maxima (setch et Gardner) Geitler,” University of Paris , France, 1966.

[2] M. Pivokonsky, J. Safarikova, M. Baresova, L. Pivokonska, I. Kopecka, A comparison of the character of algal extracellular versus cellular organic matter produced by cyanobacterium, diatom and green alga, Water Res. 51 (2014) 37–46.

[3] T. Kumar Singha, Microbial Extracellular Polymeric Substances: Production, Isolation and Applications, IOSR J. Pharm. 2 (2012) 276–281.

[4] C. Corinaldesi, R. Danovaro, A. Dell’Anno, Simultaneous recovery of extracellular and intracellular DNA suitable for molecular studies from marine sediments., Appl. Environ. Microbiol. 71 (2005) 46–50.

[5] International Humic Substances Society, Extraction of Soil Organic Matter,

[6] D. McGrath, Extraction of Organic Matter from Irish Soils, Irish J. Agric. Res. 27 (1988) 187–192.

[7] APHA, “Standard Methods for the Analysis of Water and Wastewater” Method 4500 Cl,CHLORINE (RESIDUAL), 2012.

[8] USEPA, Method 330.5: Chlorine Total Residual (Spectrophotometric, DPD).

[9] W. Gan, H. Huang, X. Yang, Z. Peng, G. Chen, Emerging investigators series: disinfection by-products in mixed chlorine dioxide and chlorine water treatment, Environ. Sci. Water Res. Technol. 2 (2016) 838–847.

[10] Palintest, Chlorine DPD 1 and 3 (Free, Total), Phot Reagents, 0 - 5 mg/L

[11] USEPA, EPA Method 300.1, Revision 1.0: Determination of Inorganic Anions in Drinking Water by Ion Chromatography, (1993).

[12] T.R. Parsons, Y. Maita, C.M. Lalli, A manual of chemical and biological methods for seawater analysis, Pergamon Press, 1984.

CHAPTER 4

WATER QUALITY DESCRIPTORS, CHLORINE REACTIVITY, AND THMs FORMATION

(This chapter consists of two sections **4a** and **4b**. **Chapter 4a** deals with the interrelationship of temporal variations in water quality parameters on chlorine reactivity with three studied water sources and corresponding formation of trihalomethanes; **Chapter 4b** deals with the discharge of chlorine residual and trihalomethanes in the chlorinated seawater effluent from Madras Atomic Power Station, Kalpakkam, India)

Chapter 4a

Comparative assessment of chlorine reactivity and trihalomethanes formation potential of three different water sources

Abstract: Trihalomethanes (THMs) are carcinogenic compounds formed during water chlorination. Nature of source water and treatment conditions significantly influence its formation. Chlorine reactivity and trihalomethanes formation potential of water samples taken from three different sources such as the sea (SWR), open reservoir (RSR), and Palar river (RVR) subsoil were assessed for a period from 2013-2017 with respect to key determinants. UV absorbance values at 254 nm (UVA_{254}) for all the water samples (n=175) varied from 0.033 to 0.09 cm^{-1} with dissolved organic carbon (DOC) content ranging between 1.08-1.88, 0.69-2.15, and 0.66-1.98 mg/L for seawater, open reservoir, and Palar subsoil water respectively. Though UV absorbance (UVA_{254}) was positively correlated with DOC content, specific UVA_{254} ($SUVA_{254}$) did not correlate with DOC. A consistent nonlinear increase in chlorine demand with increasing dose and time was observed which differed in magnitude for three water sources. THM formation potential followed the order: RSR>SWR>RVR. The seasonal average of THMs (5 mg/L dose; 24h contact time) was the highest for RSR water samples ranging from 151.62 (southwest monsoon)-198.25 µg/L (post northeast monsoon) as compared to that of the SWR (max. 105.60 µg/L) and RVR water (max. 119.66 µg/L). Among the three sources, THM in open reservoir water sample only exhibited positive correlation with its DOC. Water quality parameters such as pH, temperature, dissolved oxygen, nitrate, total nitrogen failed to establish a clear

correlation with THMs yield, which indicated the overriding influence of simultaneous occurring reactions. Among all the parameters chlorine demand appeared to be a better surrogate to predict trihalomethanes formation regardless of water sources.

4a.1 Introduction

Chlorination is one of the most used methods to disinfect drinking water and to control biofouling in industrial water utilities. Although there are many chemical processes, still chlorination is the most popular method all over the world. This is due to (1) it's strong oxidizing potential, (2) its proven effectiveness against a broad spectrum of microorganism, (3) its availability at a relatively cheaper rate and (4) its ability to provide a chlorine residual throughout the water distribution system unlike the other methods such as UV disinfection [1]. The variability of chlorine demand (CD) of water which is referred to the portion of applied chlorine consumed by the chemical and biological constituent present in natural waters makes it difficult to maintain adequate and uniform residual in the water utilities. Physico-chemical properties of water such as temperature, pH, chlorophyll, organic matter, nitrogen, etc. have a significant impact on chlorine demand. Since water quality parameters show a considerable degree of temporal variations, chlorine demand of water also fluctuates accordingly. Thus, in addition to the chlorine demand assessment, simultaneous investigation of essential factors responsible for its variations are crucial.

In spite of being the easiest and economical method of disinfection, chlorination has its disadvantages as well. Regulatory limit of chlorine in drinking water to be low and thus acute exposure is not generally expected. However, long-term exposure to chlorinated water increases the risk of cancer due to the presence of chlorination by-products in the treated water. Concerns have been expressed since mid-seventies about the apparent threat to human health due to the exposure to these toxic chlorination by-products (CBPs). The by-products formed during the reactions between chlorine and natural organic matters (NOMs) are of significant concern as they are mostly carcinogens [2–4]. CBPs formation in water is a function of several factors including temperature, pH, contact time, the concentration of bromides, residual chlorine, and NOMs [4–7]. THMs are considered as the most dominant fractions of all the by-products formed in the process of chlorination, and U.S. environmental protection agency (USEPA) has set maximum contamination level goal (MCLG) of 80 µg/L for total THMs [8]. Generally, chloroform is the dominant fraction during freshwater chlorination whereas, in seawater bromoform formed mainly with a low quantity of dibromochloromethane (DBCM) and bromodichloromethane (BDCM) [9–11]. Bromine-containing biocides are likely to produce more halogenated organics than chlorine [12] but have not been extensively studied.

Scrutiny of available literature on THM formation potential of natural water sources from India as well as from all over the world showed that studies in this regard are scanty [1,13–15]. Moreover, reports related to THM production from industrial uses of water, particularly seawater, are meagrely available. While most of the domestic need is fulfilled by fresh water source, chlorination of seawater is normal practice during its use for various purposes such as cooling water for the thermal power plant, swimming pool, desalination, and aquaculture, [9,16–19]. Atmospheric volatilization of the CBPs present in the effluents of these water utilities can also affect human health through inhalation and also results in subsequent photolysis to harmful reactive oxidants [20,21]. Most of the existing investigations on THM formation potential of natural water have been undertaken for short monitoring duration, and more of these studies are required for the results to be useful for the management of water distribution system [22]. With the above background in mind, investigations were carried out to find out the influence of temporal water quality changes on the chlorine demand and total trihalomethanes (TTHM) formation potential of three distinct types of the water source. These water sources viz. sea (SWR), Palar river subsoil (RVR) and open reservoir (RSR) available in the vicinity of the study location which are either used for potable water or industrial applications of various nuclear facilities such as Madras Atomic Power Station (MAPS), Fast Breeder Test Reactor (FBTR), Prototype Fast Breeder Reactor (PFBR) Indira Gandhi Centre for Atomic Research (IGCAR), Desalination Plants, Fast Reactor Fuel Cycle Facility (FRFCF). Details about the study area and sampling are available in the materials and methods chapter. In the present study, a comparative account of chlorine demand and TTHM formation potential of seawater, Palar sub-soil water, and Open reservoir water is provided in details. This study also explored the influence of various water quality descriptors on the magnitude of chlorine demand and the trihalomethanes formation potential.

4a.2 Results and discussion

4a.2.1 Physico-chemical characteristics

Water quality characteristics of the three water sources are given in **Table 4a. 1**. Seawater temperature ranged from 27.2 to 32.5 (29.45±1.26) ^{o}C. Temperature showed a bimodal oscillation with relatively low-temperature values during the monsoon period. The water temperature was always found to be higher in RSR water than that of Palar sub-soil water. It ranged from 24.9 to 33.6 (30.14±1.98) and 25.9 to 34.5 (30.38±2.15) ^{o}C in the RVR and RSR water respectively (**Table 4a. 1**). The apparent increase in water temperature in the case of the RSR as compared to RVR water was due to its direct exposure to atmosphere and sunlight. The pH of SWR samples ranged from 7.8 to 8.4 with an average value of 8.15±0.15. Relatively low pH was observed during the NE monsoon, and it was stable for almost the rest of the year. In the case of Palar sub-soil water, pH values ranged from 7.1 to 8.2 with the average of 7.5±0.3. The open reservoir water pH values were higher than those of the RVR water. It ranged from 7.5 to 9.7 with an average of 8.5 ± 0.5. The distinct variations in pH of these two water bodies could be attributed to the photosynthetic activity by phytoplankton and macrophytes in the reservoir leading to the increase in pH [23,24]. pH is an important parameter that significantly influences the efficiency of chlorination. At increased pH (> 8.5) most of the HOCl remains in OCl^- (95%) form and HOCl is many times more effective than OCl^- [25,26]. Conductivity (EC) of seawater ranged from 38.4-55.9 mS/cm (49.6±5.1). Relatively low EC values were observed during the NE monsoon, and the higher values were observed during summer/SW monsoon. The average EC of the RSR water was found to be higher than that of sub-soil water. It ranged from 268 to 1460 (482±200) and 143-917 (524±185) µS/cm for RVR water and RSR water respectively. Relatively low conductivity values in the RSR, as well as that of the RVR water, have coincided with NE monsoon period possibly due to the dilution caused by pure rainwater. Average value during study period showed an overall increase of about 40 µS/cm in conductivity in the open reservoir. DO content in the seawater ranged from 4.36 to 7.62 (5.9±0.75) mg/L. The open coastal water at this location is well oxygenated due to proper mixing and phytoplankton production throughout the year [27]. In aquatic systems, oxygenation is the result of an imbalance between the process of photosynthesis, degradation of organic matter and reaeration [28]. Relatively high DO values were observed in the

RSR water as compared to RVR water. It ranged from 3.33 to 6.96 (5.93±0.78) and 3.84 to 10.55 (7.72±1.55) mg/L in the RVR and RSR water samples respectively. RVR samples, being subsoil water, doesn't come in contact with atmospheric oxygen and consequently DO values were relatively low, whereas, photosynthesis in the open reservoir enhanced the DO content in water.

Nitrogenous nutrients such as nitrate, ammonia, and TN were estimated to find out their impact on chlorine demand and TTHM formation. Nitrate values ranged from BDL to 1.94 mg/L for seawater. It ranged from 0.01 to 2.09 mg/L and BDL to 0.95 mg/L for the RVR and RSR water samples respectively (**Table 4a. 1**). Its concentration in RVR water was considerably higher than the RSR water. Average ammonia concentration did not show any visible difference between SWR and RVR water. However, it was relatively low for the RSR water samples. TN concentration in the RVR water was found to be relatively high as compared to SWR and RSR water. The concentration of total nitrogen in RVR water ranged from 0.02 to 1.21 mg/L with an average of 0.26 mg/L. TN values in the RSR water varied from BDL to 0.82 mg/L with an average of 0.15 mg/L. Bromide, which is an essential parameter for the formation of THMs, was estimated for all the three water bodies. It ranged from 59.77 to 67.89 mg/L in SWR samples. The concentration of bromide observed in the RVR, and RSR water was less than 1 mg/L with very few values in the RVR water samples exceeding 1 mg/L. High nutrient content observed in the RVR water was possibly due to the residual fertilizer runoff from the surrounding agricultural land which uses both phosphate and nitrogenous based fertilizers.

Table 4a. 1 Summary statistics of physicochemical and biological parameters in the three water sources

	SWR (n=45)				PLR (n=60)				RSR (n=67)			
Variable	Min.	Max.	Mean	SD	Min.	Max.	Mean	SD	Min.	Max.	Mean	SD
pH	7.82	8.40	8.14	0.15	7.08	8.21	7.52	0.28	7.48	9.67	8.50	0.54
EC (µs/cm)	38440	55900	49590	5130	268.00	1460.0	482.92	200.84	143.00	917.00	524.84	185.18
DO (mg/L)	4.36	7.62	5.90	0.75	3.33	6.96	5.93	0.79	3.84	10.55	7.72	1.55
Temp (^{0}C)	27.20	32.50	29.45	1.26	24.90	33.58	30.14	1.98	25.90	34.50	30.38	2.15
NO_3 (µmol/l)	0.00	31.29	2.76	5.32	0.13	33.74	6.69	6.70	0.00	15.32	1.95	3.45
NH_3 (µmol/l)	0.00	6.06	2.04	1.34	0.00	13.84	2.50	2.65	0.00	7.17	1.69	1.58
TN (µmol/l)	1.45	38.22	7.80	5.86	1.45	86.32	18.71	17.37	0.00	58.31	10.43	9.61
Chl-a (mg/m^3)	0.03	8.22	2.16	1.71	0.00	4.58	0.50	0.80	1.12	18.97	6.35	4.56
Br (mg/L)	59.77	67.89	63.50	1.90	0.03	1.88	0.37	0.31	0.18	0.76	0.44	0.15
DOC (mg/L)	1.08	1.88	1.44	0.20	0.66	1.98	1.26	0.35	0.69	2.15	1.50	0.36
UVA_{254} (cm^{-1})	0.03	0.08	0.06	0.01	0.03	0.09	0.05	0.01	0.02	0.09	0.06	0.02
$SUVA_{254}$(L mg^{-1} m^{-1})	2.31	6.04	3.95	0.84	3.15	6.28	4.36	0.67	3.14	5.11	4.04	0.48

Observed significant reduction in phosphate and nitrate concentration from RVR to RSR water was due to their utilization by microorganisms and macrophytes. Phosphates and nitrates are the primary nutrient requirements for high productivity in any water body. Their presence in optimum concentrations in RVR water leads to high biological activity and extensive growth of macrophytes such as *Vallisneria, Najas* and *Ceratophyllum* in the reservoir water in the presence of sunlight, an essential element for primary production [23]. The luxuriant bio-growth in the RSR ecosystem makes it entirely a different one from the RVR subsoil water system. A recent study from the same reservoir reported an increase in organic matter content due to the growth of micro- and macrophytes substantiating our above observation on photosynthetic activity [24].

4a.2.2 Biological Parameters

Biological parameters such as chlorophyll-a, DOC, and UVA_{254} are essential descriptors for the formation of THMs, and their spatiotemporal variations affect its quantity and quality in water bodies. Chlorophyll-a, the universal pigment that forms a dominant fraction of the phytopigments, ranged from 0.03 to 8.22 mg/m^3 in seawater samples. It ranged from BDL to 4.58 mg/m^3 and 1.12 to 48.97 mg/m^3 for the RVR and RSR water respectively. The increase in chlorophyll-a content noticed in the RSR was due to the micro- and macrophyte growth in the open reservoir. UVA_{254} and the subsequently calculated $SUVA_{254}$ have been correlated with TTHM formation potential to find out the role of organics in this process. DOC values for the SWR ranged from1.08 to 1.88 mg/L with an average value of 1.44±0.20 mg/L. The RVR water DOC values (average: 126±0.35 mg/L) were marginally lower than that of the RSR (average: 1.50±0.36). The biological growth in the RSR has led to an increase in DOC content as compared to the

RVR water. The UVA_{254} values ranged from 0.033 to 0.075 cm^{-1} with an average value of 0.056±0.011 cm^{-1} for SWR samples. The corresponding $SUVA_{254}$ values ranged from 2.307-6.043 L mg^{-1} m^{-1}. The variations in UVA_{254} and $SUVA_{254}$ values in the RVR and RSR water samples were almost identical (**Table 4a. 1**). These two water sources exhibited low UVA_{254} absorption. In water, such as those containing humic fractions, it is often observed that UVA_{254} is strongly correlated to DOC content [29]. In the present study, UVA_{254} was positively correlated with DOC content in all the three water sources, in contrast, the $SUVA_{254}$ values were negatively associated with DOC in SWR and RVR water samples (**Table 4a. 2 - 4a. 4**).

4a.2.3 Chlorine demand

Chlorine demand (CD) of the water generally decides the dose required for disinfection. It is influenced by parameters like organic matter, pH, temperature, UVA_{254}, NH_3, and other inorganic compounds. CD is also a function of both time and initial chlorine dose. CD values for all the three source water types at different initial chlorine concentrations (1, 3, 5 mg/L) and time intervals (0.25 and 1 h) during the study period are given in **Figure 4a. 1**. Though not linear, consistent increase in chlorine demand with increasing dose and time was observed in all the three water sources. It ranged from 1.12 to 3.11 (1.86±0.49), 0.60 to 2.79 (1.27±0.50) and 0.89 to 2.81 (1.70±0.44) mg/L for Cl_2 dose of 5 mg/L and contact time 1 h during the chlorination of SWR (n=46), RVR (n=61) and RSR (n=68) respectively (**Table 4a. 5)**. **Figure 4a.1** also depicts the extremely variable nature of chlorine demand and a strong influence of the applied chlorine dose. The variability in CD increased at higher chlorine dose. This observation may be due to various factors such as limiting chlorine residual at lower dose and participation of resistant organic molecule at higher chlorine dose. The uncertainties in CD pose higher difficulty in predicting the chlorine demand at a higher dose than at lower dose. Comparatively low chlorine demand of the RVR water could be due to its low reactive organic matter content as compared to the other two water sources. Relatively high DOC and Chl-a content in the SWR and RSR water due to in-situ biological activities resulted in higher CD than the RSR water. CD for 1 and 3 mg/L Cl_2 doses showed a positive correlation with UVA_{254} and $SUVA_{254}$ in SWR samples. However, the correlation at 5 mg/L Cl_2 dose was insignificant. On the contrary, the CD at 5 mg/L Cl_2 dose showed a positive correlation with Chl-a content. The above observations indicated that the phytopigment might be resistant to chlorine reaction at a lower dose and reacted at a higher dose in during chlorination of SWR samples. In case of RVR and RSR water, correlations among CD at 1 & 3 mg/L dose of chlorine and UVA & SUVA were insignificant. At 5 mg/L Cl_2 dose, however, a positive correlation was observed between CD and UVA for the RVR water and CD and SUVA for the RSR water. As per the climatology of the study location, annual cycle is divided into three seasons such as southwest monsoon (SWM: June-September), northeast monsoon (NEM: October-January), post-monsoon (POM: February-May). All the data (2013-2017) were pooled into three seasons such as SWM, NEM, and POM. Seasonal variations in CD (5 mg/L dose and 1h contact time), showed a distinct trend in the case of RVR and RSR water. However, seasonal impact on the CD variation was minimum for the SWR samples (**Figure 4a. 2**). This indicates the prominent role of the reactivity of the organic matter which superseded the effect due to the temporal input of organic matter into the seawater.

Table 4a. 2 Correlation matrix (Pearson): SWR samples

Variables	pH	EC	DO	Temp	NO_3	NH_3	TN	Chl-a	Br	DOC	UVA_{254}	$SUVA_{254}$	$^1CD_{0.25}$	$^1CD_1$	$^3CD_{0.25}$	$^3CD_1$	$^5CD_{0.25}$	$^5CD_1$
pH	**1**																	
EC (µs/cm)	**-0.545**	**1**																
DO (mg/L)	**-0.262**	**0.688**	**1**															
Temp (^{0}C)	-0.158	**0.366**	0.065	**1**														
NO_3 (µmol/l)	0.040	0.212	**0.336**	-0.097	**1**													
NH_3 (µmol/l)	0.144	-0.164	**-0.259**	-0.157	0.121	**1**												
TN (µmol/l)	0.146	0.103	0.202	-0.057	**0.864**	0.118	**1**											
Chl-a (mg/m^3)	**-0.311**	0.201	0.118	**0.270**	0.068	-0.044	-0.025	**1**										
Br (mg/L)	0.001	**0.444**	**0.447**	**0.349**	0.102	-0.181	0.083	0.206	**1**									
DOC (mg/L)	**0.267**	-0.182	-0.059	-0.091	0.076	0.054	0.215	0.012	0.013	**1**								
UVA_{254} (cm^{-1})	0.078	-0.184	0.068	-0.160	-0.106	-0.138	0.010	-0.101	0.165	**0.294**	**1**							
$SUVA_{254}$	-0.104	-0.077	0.075	-0.080	-0.157	-0.138	-0.127	-0.092	0.137	**-0.344**	**0.788**	**1**						
$^1CD_{0.25}$	0.038	-0.182	0.081	-0.113	-0.148	-0.019	-0.178	-0.010	0.174	0.057	**0.631**	**0.570**	**1**					
$^1CD_1$	0.095	**-0.296**	0.017	-0.214	-0.170	0.005	-0.240	-0.088	0.031	0.204	**0.618**	**0.472**	**0.855**	**1**				
$^3CD_{0.25}$	-0.077	0.039	**0.261**	-0.039	0.167	0.042	0.071	0.198	0.223	-0.013	**0.303**	**0.305**	**0.615**	**0.583**	**1**			
$^3CD_1$	-0.144	0.113	**0.283**	-0.056	0.087	-0.013	-0.026	0.246	**0.304**	-0.044	**0.261**	**0.277**	**0.486**	**0.506**	**0.865**	**1**		
$^5CD_{0.25}$	-0.227	0.085	0.234	0.018	0.085	-0.155	0.009	**0.413**	0.242	0.003	0.237	0.234	**0.476**	**0.447**	**0.897**	**0.848**	**1**	
$^5CD_1$	**-0.294**	0.205	**0.309**	-0.081	0.161	-0.013	-0.037	**0.297**	0.220	-0.096	0.158	0.213	**0.360**	**0.371**	**0.752**	**0.871**	**0.776**	**1**
$^1TTHM_{0.5}$	-0.147	-0.024	0.135	0.055	-0.164	-0.213	-0.207	0.100	0.224	0.048	**0.697**	**0.630**	**0.885**	**0.766**	**0.494**	**0.437**	**0.424**	**0.386**
$^1TTHM_{24}$	-0.097	-0.108	0.036	0.027	-0.193	-0.193	-0.234	0.103	0.155	0.053	**0.682**	**0.611**	**0.816**	**0.737**	**0.430**	**0.366**	**0.343**	**0.352**
$^3TTHM_{0.5}$	-0.062	-0.088	0.077	0.056	-0.201	-0.169	-0.237	0.139	0.209	0.061	**0.705**	**0.625**	**0.761**	**0.655**	**0.457**	**0.429**	**0.367**	**0.403**
$^3TTHM_{24}$	-0.050	-0.072	-0.053	0.095	-0.121	-0.165	-0.140	0.027	0.047	0.051	**0.584**	**0.504**	**0.551**	**0.419**	0.171	0.078	0.097	0.144
$^5TTHM_{0.5}$	0.041	-0.065	-0.107	0.043	-0.010	0.030	0.003	0.069	-0.058	0.060	**0.493**	**0.408**	**0.340**	**0.266**	0.035	0.009	-0.054	0.074
$^5TTHM_{24}$	-0.143	0.075	0.071	0.092	-0.055	-0.105	0.006	0.116	0.045	0.096	**0.570**	**0.456**	**0.344**	0.235	0.045	0.011	0.037	0.101

Values in bold are significantly different from 0 with a significance level alpha=0.1; $SUVA_{254}$ in L mg^{-1} m^{-1}, CD in mg/L and TTHM in µg/L

Table 4a. 3 Correlation matrix (Pearson): RVR water

Variables	pH	EC	DO	Temp	NO_3	NH_3	TN	Chl-a	Br	DOC	UVA_{254}	$SUVA_{254}$	$^{1}CD_{0.25}$	$^{1}CD_{1}$	$^{3}CD_{0.25}$	$^{3}CD_{1}$	$^{5}CD_{0.25}$	$^{5}CD_{1}$
pH	**1**																	
EC (µs/cm)	0.213	**1**																
DO (mg/L)	-0.019	0.178	**1**															
Temp (^{0}C)	-0.140	-0.136	0.110	**1**														
NO_3 (µmol/l)	-0.134	-0.131	**-0.312**	-0.106	**1**													
NH_3 (µmol/l)	-0.005	0.200	-0.078	-0.118	-0.238	**1**												
TN (µmol/l)	-0.163	-0.086	-0.035	**-0.309**	**0.551**	0.036	**1**											
Chl-a (mg/m^3)	**0.253**	**0.348**	0.113	-0.225	0.206	-0.019	**0.386**	**1**										
Br (mg/L)	0.133	**0.745**	0.112	-0.072	**-0.256**	0.194	-0.169	0.068	**1**									
DOC (mg/L)	-0.054	**0.314**	0.059	-0.086	0.094	0.082	-0.032	0.096	**0.283**	**1**								
UVA_{254} (cm^{-1})	0.095	**0.428**	0.012	-0.131	0.108	0.083	-0.021	0.198	**0.336**	**0.837**	**1**							
$SUVA_{254}$	**0.248**	0.090	-0.030	-0.066	-0.018	0.008	-0.012	0.083	-0.004	**-0.416**	0.130	**1**						
$^{1}CD_{0.25}$	-0.102	0.075	-0.032	0.001	-0.033	0.140	0.083	0.076	0.124	0.048	0.160	0.161	**1**					
$^{1}CD_{1}$	-0.025	0.067	-0.004	-0.015	-0.015	0.088	0.032	0.043	0.119	0.085	0.193	0.166	**0.819**	**1**				
$^{3}CD_{0.25}$	-0.073	0.041	-0.017	0.116	-0.014	0.021	0.055	0.015	0.057	0.004	0.092	0.137	**0.922**	**0.812**	**1**			
$^{3}CD_{1}$	-0.107	-0.033	-0.020	0.173	-0.070	0.006	-0.020	-0.048	0.039	0.013	0.080	0.119	**0.865**	**0.827**	**0.912**	**1**		
$^{5}CD_{0.25}$	**-0.263**	0.149	0.192	0.077	-0.152	0.108	-0.008	0.126	0.149	**0.287**	**0.282**	-0.047	**0.615**	**0.618**	**0.584**	**0.558**	**1**	
$^{5}CD_{1}$	**-0.297**	0.131	0.089	0.043	-0.030	0.144	0.006	0.130	0.119	**0.260**	0.249	-0.040	**0.647**	**0.673**	**0.642**	**0.623**	**0.936**	**1**
$^{1}TTHM_{0.5}$	-0.002	0.128	-0.054	-0.082	-0.119	0.199	-0.065	0.027	0.162	0.030	0.160	0.177	**0.796**	**0.786**	**0.731**	**0.702**	**0.570**	**0.603**
$^{1}TTHM_{24}$	0.124	**0.263**	0.041	0.129	-0.197	0.124	-0.172	-0.115	0.224	-0.026	0.027	0.049	**0.480**	**0.528**	**0.547**	**0.497**	**0.398**	**0.385**
$^{3}TTHM_{0.5}$	0.070	0.064	-0.138	0.060	0.036	0.020	-0.031	0.005	0.077	-0.015	-0.042	-0.082	**0.493**	**0.404**	**0.513**	**0.418**	0.102	0.182
$^{3}TTHM_{24}$	0.078	-0.091	-0.072	0.143	-0.076	-0.047	-0.174	-0.134	0.009	-0.044	-0.165	-0.191	0.159	0.167	0.208	0.166	-0.014	0.006
$^{5}TTHM_{0.5}$	0.130	-0.112	-0.096	-0.121	0.098	-0.010	-0.032	-0.028	-0.055	0.048	-0.001	-0.061	**0.325**	**0.327**	**0.333**	0.252	-0.012	0.059
$^{5}TTHM_{24}$	0.099	-0.092	-0.044	-0.023	0.124	-0.085	0.008	-0.040	-0.090	-0.029	-0.113	-0.120	0.062	0.050	0.137	0.031	-0.188	-0.149

Values in bold are significantly different from 0 with a significance level alpha=0.1, $SUVA_{254}$ in L mg^{-1} m^{-1}, CD in mg/L and TTHM in µg/L

Table 4a. 4 Correlation matrix (Pearson): RSR water

Variables	pH	EC	DO	Temp	NO_3	NH_3	TN	Chl-a	Br	DOC	UVA_{254}	$SUVA_{254}$	$^1CD_{0.25}$	$^1CD_1$	$^3CD_{0.25}$	$^3CD_1$	$^5CD_{0.25}$	$^5CD_1$
pH	**1**																	
EC (µs/cm)	**-0.358**	**1**																
DO (mg/L)	**-0.223**	0.068	**1**															
Temp (^{0}C)	0.141	**0.290**	-0.121	**1**														
NO_3 (µmol/l)	-0.180	-0.106	0.174	**-0.219**	**1**													
NH_3 (µmol/l)	-0.025	0.003	-0.021	0.129	0.016	**1**												
TN (µmol/l)	-0.007	**-0.250**	0.079	-0.190	**0.336**	**0.229**	**1**											
Chl-a (mg/m^3)	-0.093	**-0.229**	**0.379**	**-0.278**	**0.284**	-0.173	**0.311**	**1**										
Br (mg/L)	**-0.341**	**0.795**	0.027	**0.208**	-0.145	-0.060	**-0.299**	**-0.289**	**1**									
DOC (mg/L)	**-0.229**	0.170	0.163	**-0.211**	0.075	0.006	-0.066	0.073	0.102	**1**								
UVA_{254} (cm^{-1})	**-0.237**	**0.243**	0.180	-0.147	0.072	-0.033	-0.098	0.085	0.180	**0.906**	**1**							
$SUVA_{254}$	-0.081	**0.227**	0.066	0.074	0.019	-0.076	-0.094	0.024	**0.243**	0.142	**0.540**	**1**						
$^1CD_{0.25}$	0.178	-0.009	-0.108	0.159	-0.201	-0.169	-0.150	-0.107	0.051	-0.182	-0.128	0.081	**1**					
$^1CD_1$	0.181	-0.019	-0.091	0.139	-0.091	-0.153	-0.103	-0.068	0.040	**-0.206**	-0.163	0.055	**0.928**	**1**				
$^3CD_{0.25}$	**0.232**	-0.055	-0.064	0.145	-0.184	-0.083	-0.025	0.080	-0.066	-0.189	-0.094	0.161	**0.890**	**0.814**	**1**			
$^3CD_1$	**0.238**	-0.193	-0.007	0.189	-0.007	-0.095	-0.004	0.173	-0.132	-0.103	-0.002	0.191	**0.596**	**0.575**	**0.742**	**1**		
$^5CD_{0.25}$	0.074	0.023	0.057	0.165	**-0.311**	-0.076	-0.127	0.075	0.074	-0.038	0.078	**0.257**	**0.370**	**0.320**	**0.401**	**0.462**	**1**	
$^5CD_1$	0.193	-0.136	-0.052	0.113	-0.191	-0.041	-0.152	0.028	0.016	-0.012	0.045	0.143	**0.383**	**0.380**	**0.389**	**0.572**	**0.829**	**1**
$^1TTHM_{0.5}$	-0.010	0.057	0.197	-0.108	-0.023	-0.059	**-0.252**	0.024	0.038	**0.574**	**0.706**	**0.501**	0.011	-0.059	0.047	0.158	0.006	-0.028
$^1TTHM_{24}$	-0.169	0.019	**0.242**	-0.110	0.072	0.023	-0.165	-0.074	0.004	**0.496**	**0.564**	**0.331**	-0.144	-0.158	-0.176	-0.139	-0.141	**-0.236**
$^3TTHM_{0.5}$	0.006	0.060	-0.072	0.032	0.023	-0.024	**-0.260**	-0.185	0.088	**0.253**	**0.298**	0.179	-0.146	-0.192	-0.163	-0.090	-0.146	-0.146
$^3TTHM_{24}$	0.008	0.041	-0.030	-0.146	-0.096	-0.068	**-0.236**	-0.198	0.007	**0.311**	**0.330**	0.140	-0.182	-0.142	**-0.218**	-0.199	-0.127	-0.132
$^5TTHM_{0.5}$	0.038	0.005	-0.039	0.116	0.050	-0.101	**-0.240**	-0.163	-0.043	0.117	0.091	-0.039	-0.107	-0.110	-0.139	-0.110	**-0.329**	**-0.275**
$^5TTHM_{24}$	0.039	0.028	-0.125	0.121	-0.005	-0.119	-0.176	-0.154	-0.099	0.190	0.163	0.001	-0.152	-0.126	-0.139	-0.119	**-0.277**	**-0.256**

Values in bold are significantly different from 0 with a significance level alpha=0.1; $SUVA_{254}$ in L mg^{-1} m^{-1}, CD in mg/L and TTHM in µg/L

Table 4a. 5 Summary statistics of chlorine demand (mg/L) and TTHM (µg/L) content in the three water sources

	SWR (n=45)				PLR (n=60)				RSR (n=67)			
Variable	Min.	Max.	Mean	SD	Min.	Max.	Mean	SD	Min.	Max.	Mean	SD
$^1CD_{0.25}$	0.31	0.72	0.48	0.11	0.06	0.76	0.25	0.15	0.22	0.72	0.44	0.12
$^1CD_1$	0.50	0.99	0.74	0.13	0.32	1.00	0.54	0.17	0.62	1.00	0.83	0.11
$^3CD_{0.25}$	0.44	2.21	0.87	0.36	0.14	1.21	0.41	0.24	0.30	1.09	0.65	0.20
$^3CD_1$	0.75	2.47	1.31	0.39	0.38	1.56	0.81	0.27	0.48	2.24	1.10	0.30
$^5CD_{0.25}$	0.76	2.54	1.20	0.33	0.18	1.89	0.79	0.40	0.47	1.98	1.18	0.32
$^5CD_1$	1.12	3.11	1.86	0.49	0.60	2.79	1.27	0.50	0.89	2.81	1.70	0.44
$^1TTHM_{0.5}$	18.66	37.66	27.55	5.34	15.68	24.51	18.46	1.97	14.56	38.69	25.48	5.46
$^1TTHM_{24}$	32.69	68.95	50.19	9.13	28.96	50.26	36.78	4.55	35.66	101.22	66.24	15.28
$^3TTHM_{0.5}$	31.56	75.69	52.65	9.27	18.66	55.66	32.96	9.44	19.89	60.99	36.44	9.36
$^3TTHM_{24}$	36.89	88.65	63.04	12.03	51.26	133.86	86.87	20.23	55.75	202.33	103.92	30.93
$^5TTHM_{0.5}$	40.22	96.22	66.19	12.48	24.42	86.51	44.24	13.55	24.29	93.53	50.60	15.87
$^5TTHM_{24}$	68.23	156.22	111.06	20.09	64.71	198.24	113.18	26.20	77.14	356.22	178.58	49.52

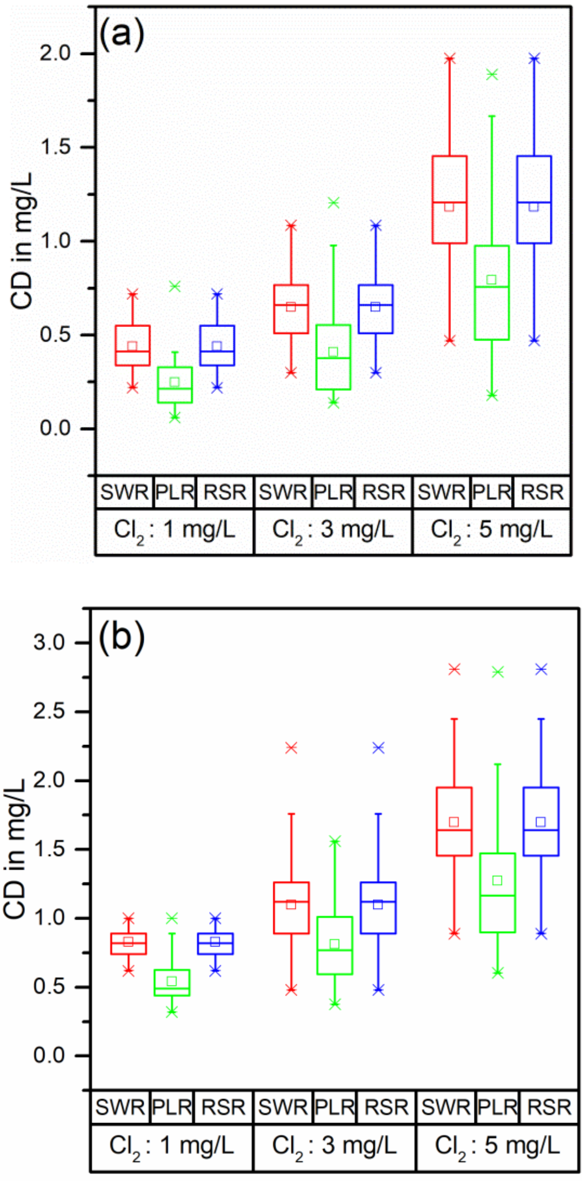


Figure 4a. 1 (a) & (b) Comparison of chlorine demand variation in different sources of water at different dose of chlorine and contact time ((a: 0.25 h, (b): 1 h) (SWR: n=45; PLR: n=60; RSR: n=67

The increase in CD for RVR and RSR water during NEM and post-NEM period could be ascribed to the increase in biological growth during these periods in the presence of optimal nutrient concentration in the water sources. On the other hand, the CD of SWR was relatively high during the SWM and NEM as compared to that of the RVR and RSR water. It showed that despite the allochthonous inputs during the monsoon season, the dynamics of the coastal water helped to maintain its homogeneity in the physicochemical and biological properties.

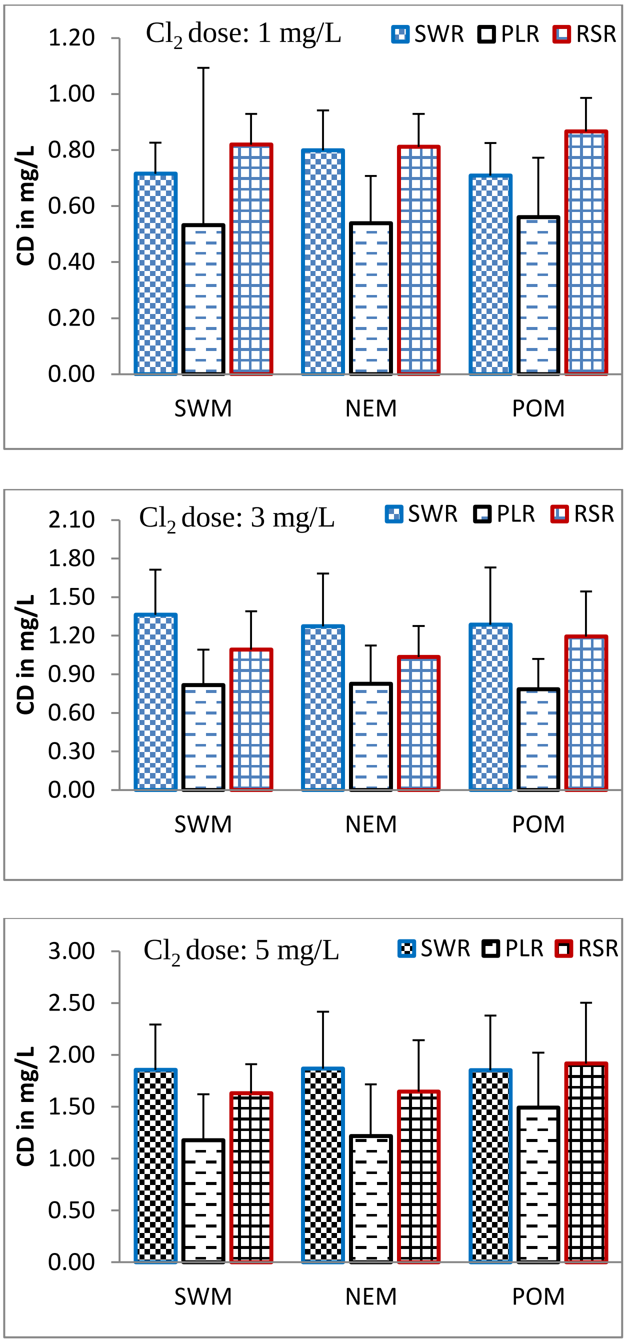


Figure 4a. 2 Seasonal variations (2013-2017) in chlorine demand of different water sources at chlorine dose of 1, 3 and 5 mg/L and 1 h contact time

4a.2.4 TTHM formation potential

Critical factors that influence the formation of THMs include contact time, CD, temperature, pH, the concentration of precursors, and bromide ions. There was considerable disparity in these parameters observed for three different water sources which had significantly affected the load and distribution of THMs. Similar to that of CD, a linear increase in total THMs level was observed for different chlorine doses and contact times (**Figure 4a. 3**). Among the three water sources, RSR water samples were found to have the highest THMs formation potential (**Table 4a. 5**). As expected, the RVR water, which had relatively low DOC, Chl-a, UVA_{254} level, had the lowest THM formation potential. The TTHMs levels for 0.5 h contact time were relatively high for all the chlorine doses in the chlorinated SWR samples as compared to that for chlorinated RSR water samples, whereas, after 24 h contact time THMs trend was opposite. It indicates that the TTHM formation is not only dependent on the amount of organic matter, but also it depends upon the types of organic matter present in water. It can also be inferred that fraction of fast reactive organic matter was more in the SWR among the three water sources which resulted in an initial high load of THMs in SWR and attained a plateau quickly compared to RVR and RSR water samples. Temporal variations in TTHM at different chlorination conditions are given in **Figure 4a. 4**. It showed that TTHM contents were always higher for RSR water than for SWR and RVR water samples at all the chlorine doses and contact times. The seasonal average values of THMs for RSR water samples (for a 5 mg/L dose; 24h contact time) ranged from 151.62-198.25 µg/L, the highest and the lowest being observed during SWM and post-NEM season. Seasonal variations in TTHM for SWR and RVR water samples, for the above conditions, were within 105.60-119.66 µg/L. In SWR samples, TTHM obtained for all experimental conditions showed a positive correlation with CD values observed at 1 mg/L chlorine dose. The associations became insignificant among TTHM and CD at higher doses. Similarly, in RVR water samples, TTHM formed for chlorine dose of 1 mg/L (0.5 & 24 h), 3 mg/L (0.5 h) and 5 mg/L (0.5 h) were positively correlated with all the values of the CD.

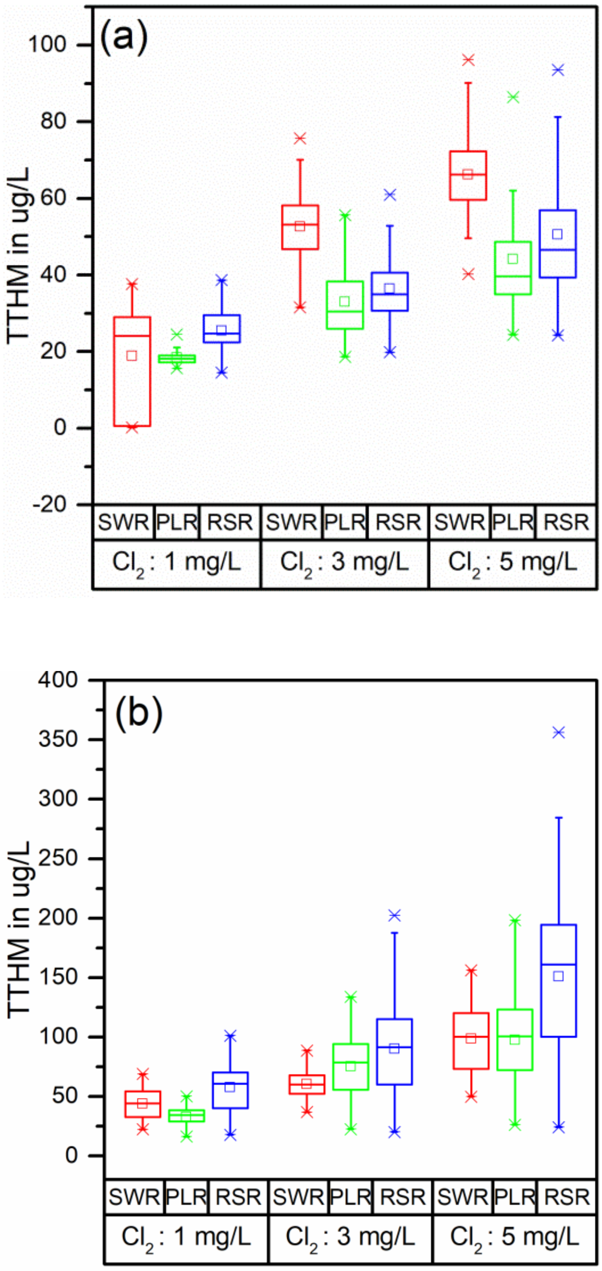


Figure 4a. 3 (a) & (b) TTHM formation potential characteristics of different source water at different dose of chlorine and reaction time ((a): 0.5 h, (b): 24 h) (SWR: n=45; PLR: n=60; RSR: n=67)

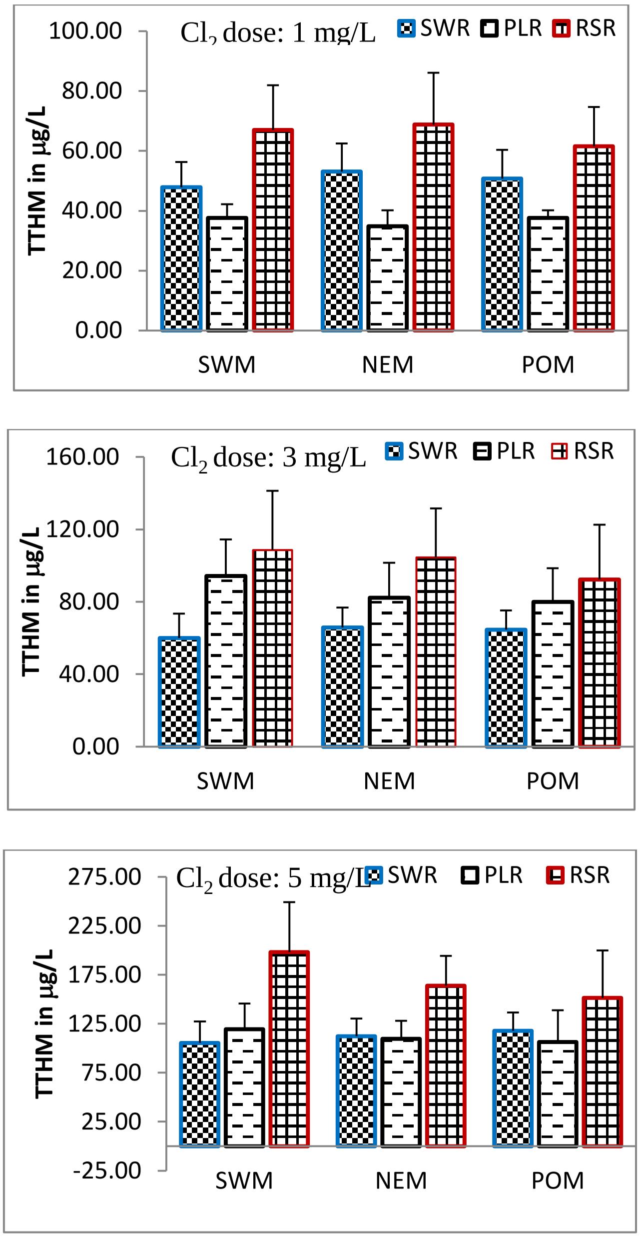


Figure 4a. 4 Seasonal variations (2013-2017) in TTHM formation potential of different sources at chlorine dose of 1, 3 and 5 mg/L and 24 h contact time.

Interestingly, the TTHM content and CD values in the Open reservoir did not show any positive correlation, unlike the other two water sources. Moreover, a few negative associations between TTHM and CD were observed in the RSR samples indicating the frequent occurrence of organic matter input which was not the active THM precursors and chlorine was consumed via other oxidative reactions. Although TTHM formation potential of the RSR was high, the magnitude of TTHM formation was not quantitatively reciprocated with the increase in the CD. It indicates the presence of non-THM-forming precursor constituents in the organic content of RSR water. The above observation was supported by the fact that, TTHM contents in the RSR showed a positive correlation with DOC, which was not observed in the other two water sources. Biochemical composition of algal matters is reported to play a vital role in determining the TTHM yield [30]. Previous studies have shown higher TTHM formation potential of water bodies with diatoms than green algae under the same chlorination conditions [31]. Aquatic humic acids contain more aromatic carbon than algal-derived carbon, and therefore have higher TTHM formation potential [32]. The above reasons possibly explain the observation of the non-collinear behavior of CD and TTHM content in the RSR water. However, CD had a substantial effect on the overall yield of TTHM in all the natural water studied (**Figure 4a. 5**). As the chlorine dose is increased, chlorine reacted with organic matter via otherwise unfavorable oxidative reactions rather than reactions leading to THMs formation. It might have led to the non-collinearity between CD and TTHM formation potential as the chlorine dose was increased. UVA_{254} and $SUVA_{254}$ values, which serve as a proxy for aromatic contents in the DOC, were positively correlated with TTHM for all doses and all contact times in the SWR samples. However, in the RVR water, all the correlations among the above parameters were insignificant indicating the negligible presence of organic materials contributing to UVA_{254}. On the contrary, in the RSR samples, UVA_{254} was selectively correlated positively with TTHM levels at 1, and 3 mg/L dose and the $SUVA_{254}$ was positively correlated with TTHM contents only for

1 mg/L dose. The above observations could be attributed to the characteristics of organic matter which is determined by its nature of origin. While DOC from aquatic algae has relatively large nitrogen content, low aromatic carbon, and low phenolic contents; terrestrially-derived DOC is relatively deficient in nitrogen content but abundant in aromatic and phenolic components. It suggests that the aromatic fraction of organic matter, which was postulated to be the most reactive precursor, varies considerably with the source of origin [33]. The longer hydrologic residence time (typically in the order of months to years) may also be long enough to allow the transformation of the nature of DOC either from external sources or in-situ generation by organisms [34]. Many studies which have correlated UVA_{254} and $SUVA_{254}$ with the TTHM have suggested that with low to a moderate value of UVA_{254}, the usefulness of these parameters as a surrogate for prediction of TTHM formation is limited [35,36]. The selective positive correlations between TTHM and UVA_{254} observed in the present study could be due to the presence of some particular organic matter, most probably of non-humic, non-UV absorbing, and hydrophilic nature, in these water sources. These fractions possibly comprised only a small portion of all organic matter due to which TTHM did not show a positive correlation with DOC especially in the SWR and RVR water samples. TTHM in the Open reservoir water showed a negative correlation with TN content. Many studies have reported the increased formation of THMs in the chlorinated water due to the presence of bromide [37–40]. However, the extent of increase is strongly affected by various parameters such as reaction time, chlorine dose, temperature and pH [41,42]. In the present study, the Pearson correlation matrix did not show any significant correlation between THM level and bromide concentration in all the three water sources (**Table 4a. 2 - 4a. 4**).

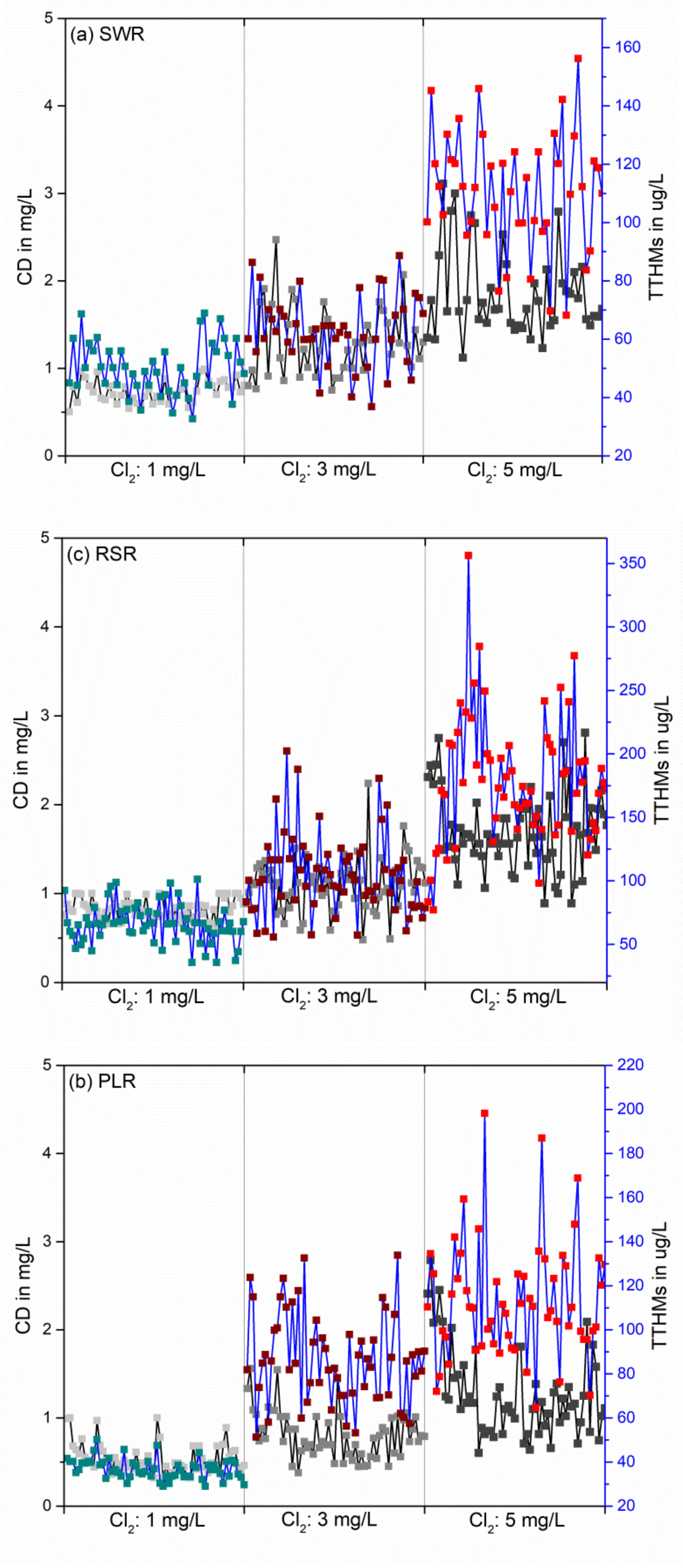


Figure 4a. 5 Trend of chlorine demand variation with that of variation in trihalomethanes formation potential of different source water.

In seawater samples, lowest of the bromide level (59.7 mg/L) observed during the study was also in excess and sufficient to instantly reduce all the chlorine at studied chlorine concentrations (1-5 mg/L). Thus, its temporal variation did not shift the oxidant equilibrium (HOCl ↔ HOBr) much and thus had an insignificant role in the change of TTHM level. For RVR and RSR water, other competitive reactions might have played more influential role overriding the effect of bromide on the yield of TTHM. Though the addition of bromide to the experimental samples generally resulted in higher TTHM formation [43], it was not straightforward to ascribe temporal variations of bromide with the higher yield of THMs in case of our real water samples. Similarly, for other parameters, many studies had attempted to experimentally quantify their effect on the THMs yield under laboratory conditions. However, natural temporal variations of these parameters of real water samples failed to establish a clear correlation with the overall THMs yield due to the complexity of simultaneously occurring interdependent reactions.

4a.3 Conclusion

Distinct variations in chlorine demand and total THMs formation was observed for the three water sources studied. Water quality descriptors such as pH, temperature, bromide, etc. failed to establish a strong correlation with chlorine demand and trihalomethanes formation potential due to the numerous simultaneous occurring reactions. Though, UVA_{254}, $SUVA_{254}$, DOC, etc. have been proven as useful surrogate for the prediction of THM formation during laboratory experiments, the randomness of temporal variations in the reactivity of DOC in real water samples observed during our study made these parameters less useful for the universal prediction of THMs formation in the three studied water sources. Chlorine demand in conjunction with other water quality descriptors seemed to be a better alternative surrogate to predict the THM yield capacity of the water. All the three biogeochemically distinct water sources such as SWR, RVR, and RVR water were susceptible to the formation of the significant amount of THMs and followed the order: RSR> SWR > RVR. Variability in chlorine demand was more affected by chlorine dose, and the extent of temporal variations was comparable for all the three types of water studied. Chlorine demand of the RVR water was the lowest followed by SWR, and the highest was observed for RSR water. RVR and RSR water showed the maximum seasonal variations in THMs formation compared to SWR for low chlorine dose up to 3 mg/L.

Chapter 4b

Monitoring chlorine residual and trihalomethanes in the chlorinated seawater effluent of Madras Atomic Power Station, Kalpakkam, Tamil Nadu

Abstract: Periodic sampling of the discharged seawater effluent from Madras Atomic Power Station (Kalpakkam, Tamil Nadu, India) was carried out during the period 2013-2017 to assess the residual chlorine and trihalomethanes content in the outfall discharge water. The variations in dissolved oxygen, temperature, and pH were correlated with the residual chlorine and trihalomethanes content in the discharged effluent. The difference in temperature (ΔT) between influent and effluent seawater samples ranged from 1.95-11.0^{0}C (6.47±1.87). More than 95% of the ΔT values were within the guideline value of 7^{0}C. The discharge water was associated with a marginal reduction in DO content and a marginal increase in conductivity values. The total residual chlorine contents in the discharged seawater outfall ranged from 0.06-0.42 (0.16±0.08) mg/L which was within the stipulated values of 0.5 mg/L. Trihalomethanes values were ell within the stipulated limit and ranged from 0.04-65.03 (13.06±14.38) µg/L. In addition to bromoform as the major constituent, occurrence of significant amount chloroform was observed occasionally in the discharge water.

4b.1 Introduction

Most industrial production processes such as refineries, petrochemical plants, thermal power plant including nuclear power plant need cooling water for efficient and intermittent operation [44]. Typically, a 500 MW (e) nuclear power plant uses about 30 $m^3 s^{-1}$ of cooling water to extract heat from the condenser and other auxiliary heat exchanger systems for its efficient operation [45,46]. Due to this huge requirement of condenser cooling water, nuclear power plants are preferably located near the coast and generally adopts once-through cooling (OTC) water systems. The use of seawater has its disadvantages, biofouling being the most important one. Colonization of fouling organisms on the various surfaces of the cooling water system (CWS) such as intake structures, screens, pumps, condenser tubes, heat exchangers, etc. greatly hamper the smooth operation of the plant resulting in a reduction of heat transfer efficiency. Unless controlled, biofouling adversely affects the power plant in term of efficiency and structural damage which may lead to even unsafe conditions [47]. Hence, biofouling control has been a prime issue for coastal power plant operation throughout the world.

Chlorination is the most commonly used method for biofouling control in many power stations. Previous studies have concluded that it could cause adverse effects on organisms even at low-level discharge from power plants [48] of course with contradictory results [49]. Chlorination toxicity observed to have a more pronounced effect on phytoplankton affecting various physiological and metabolic processes [50,51]. Moreover, the formation of chlorination by-products (CBPs) during chlorination is also of profound concern due to their toxicity [52–54]. Both residual chlorine and the CBPs pose threats to marine ecosystem even if their concentration remains low as the quantity of treated water release is copious [55]. It also can affect human health on exposure due to its volatilization and subsequent formation of reactive oxidant [21]. THMs are the most dominant fractions of all the CBPs formed. The formation of CBPs has been extensively studied, primarily concerned with fresh water sources and distribution utilities for drinking water supply. However, in marine environments, limited information is available on CBPs formation, which again mainly focussed on seawater desalination followed by nuclear power [11,55–57]. Further, such studies from India are limited [9,58]. A comprehensive understanding of the CBPs flux in industrialized embayment are required to evaluate their possible impact on the ecosystem. Considering the lack of data from India and the health risk associated with CBPs, the present study was carried out during the period 2013-2017 to investigate the load and species distribution of THMs in the effluent of Madras Atomic Power Station (MAPS), India. Temperature, pH, DO, conductivity, chlorine demand, trihalomethanes formation potential, etc. were also periodically monitored to evaluate the effect of their temporal variations on the THMs and residual chlorine discharge. The main objectives of this study were to (i) asses residual Cl_2 and THMs content in the MAPS discharge seawater to ensure the compliance of environmental stipulations, (ii) monitor ΔT of influent and effluent seawater, (iii) find out correlation between residual chlorine and THMs and (iv) evaluate the influence of source seawater pH, temp, DO, salinity on the THMs content in the effluent. Moreover, it is also planned to use the results of the present study in predicting THM yield and optimization of chlorine use during the chlorination of seawater.

4b.2 Biofouling at MAPS and chlorination regime

Attachment and subsequent growth of sessile communities on manmade structures is known as biofouling. Worldwide economic loss arising because of biofouling has been estimated to be billions of rupees [59]. Power plants are generally set up in the coastal regions to meet the huge water requirement for cooling purposes [46]. However, use of seawater has its own disadvantage mainly the occurrence of biofouling which impacts the plant performance. Various metal and concrete structures of the cooling system provide a suitable substrate for the settlement and growth of marine organisms. A continuous supply of oxygen and food, low siltation, lack of competition and low predation pressure favors the luxuriant growth of fouling organisms in the cooling water system. These fouling organisms directly or indirectly affect the plant efficiency, structural integrity and safety of nuclear plants [47]. The impact of biofouling on manmade marine structures is staggering with respect to efficiency and structural damage. Hence the biofouling control is a routine practice for the efficient operation of the power station.

Biofouling is a universal problem with respect to the cooling system of coastal power plants. Impacts of biofouling on the cooling conduits of coastal power plant from all over the world have been studied by several researchers since long [60–64]. Though studies in this regard from different parts of India are scarce, it has been immensely studied at Kalpakkam coast due to the existing Madras Atomic Power Station (MAPS) [65–67]. Macrofouling has been recognized as a serious issue in the cooling water system of MAPS. The pre-condenser cooling water structure (tunnel, intake and forebay shafts) supports heavy settlement of benthic organisms such as barnacles, mussels, oysters, ascidians and hydroids, etc. Biofouling had affected the cooling system and performance of the plant adversely [66,68,69]. Investigation on the fouling problems of MAPS cooling system has shown extensive settlement of macro-benthic organisms inside the tunnel, which was calculated to be around 580 tonnes [70], that caused severe pressure drops in the cooling circuits. The fouling organisms formed a thick layer of maximum of 25 cm with an average of 18 cm in the intake tunnel [66]. Additionally, a huge growth of macro-foulant on the intake screen has also affected the plant operation. In the condenser section, clogging of tubes by dead green mussel has also been reported that affected the plant performance [71].

A number of biofouling control strategies have been developed constituting various physical and chemical methods. A general solution to biofouling problem is not feasible due to various factors like the nature of aquatic life, submerged structures, physically inaccessible portions of designed structures, etc. Though most biofouling control strategies aim to deter the initial settlement of larval and juvenile stages of biofoulers. In addition, selection of control measures is also governed by factors like efficiency, cost and environmental acceptability. Although various physical methods like Amertap, sponge ball, mesh screens, heat treatment, and different biocides are in use for biofouling control, chlorination stands out as the most widely used and efficient method due to its proven effectiveness, easy availability and relatively low cost. From the first use of chlorination for biofouling control of cooling water by Commonwealth Edison Company's Northwest Station in 1924, it has become the most widely used mechanism of biofouling control till the recent times. US Environmental Protection Agency (USEPA) and other national/international regulatory agencies have issued guidelines on allowable chlorine, and chlorination byproducts discharge to minimize its possible toxicity to the aquatic organism [60]. MAPS has been using a low dose continuous chlorination regime since its commissioning since the early 1980s [71]. As hard-bodied organisms like green mussels and barnacles are dominant at Kalpakkam, low dose continuous chlorination with weekly boosters has been found as the optimum control method for this coastal site. Because of the persistent availability of the desired residual level in the cooling water system during continuous chlorination, it fairly succeeded in overcoming both microfouling in the condenser and macrofouling in the pre-condenser sections. Seawater drawn for MAPS condenser cooling is chlorinated at the intake point, and the treated water is discharged back to sea through an 800 m long artificial canal. There are 8 condenser cooling water pumps (CCWP) and 4 process seawater pumps (PSWP) with a cooling water drawing capacity of 11,300 and 9600 m^3h^{-1} respectively. When all pumps are in operation, the cooling water travels at a speed of 2-2.5 m s^{-1} and the cooling seawater takes approximately 5–7 min to travel from the intake to the outfall discharge. The cooling water temperature increases to about 7-10^0C across the heat exchanger. Chlorine as Cl_2 gas is added at a rate of 15-20 kg pump-^{1} h^{-1} continuously at intake [49]. This continuous low dose chlorination regime has been adopted in MAPS power plant aiming a chlorine dose of 1 mg/L to the cooling water to maintain a residual level of 0.2–0.5 mg/L at the discharge outlet [49].

4b.2 Results and Discussion

4b.2.1 Water quality characteristics

Ambient seawater temperature (^{o}C) at intake during the study period of 2013-2017 ranged from 27.4 to 32.5 (29.53±1.17) ^{o}C, whereas, after extracting the waste heat from the condenser, the temperature at outfall discharge ranged from 31.3 to 40.7

(36.19±1.77) ^{o}C. The difference in temperature (ΔT) between water samples collected at Intake and outfall ranged from 1.95 to 11.0 (6.47±1.87) ^{o}C (**Figure 4b. 1**). The wide variation in ΔT observed at the outfall discharge was essentially due to the variations in intake temperature as well as variations in operating power level of the reactor. A further reduction of about 2 ^{o}C in discharge water temperature (31.2-37.1; Average: 34.22±1.33 ^{o}C) was observed near the mixing point (**Figure 4b. 2**), due to the heat dissipation to the atmosphere along the engineered canal. Temperature always acts as a covariate rather than as an independent factor [72], and it influences almost every biochemical interaction and chemical reaction in water masses. Increase in water temperature results in an exponential rise in the reaction rates, both for oxidation and by-products formation reactions. Increasing temperature also generally favors the formation of CBPs such as THMs. Though the reaction time of chlorine and the temperature of a cooling system may not change considerably over a period, it is the nature of source water that determines the temporal variation in types of by-products formed. Thus, at the same temperature, the qualitative and quantitative composition of CBPs will vary based on source water which itself undergoes seasonal changes.

pH of seawater ranged from 7.7 to 8.4 with an average value of 8.06±0.21. Relatively low pH was observed during the NE monsoon, and it was stable for almost the rest of the year. The outfall discharge water pH ranged from 7.6 to 8.4 (7.98±0.18) with negligible change as compared to that of the intake water (**Figure 4b. 3**). pH is one of the essential parameters that significantly influences the efficiency of chlorination. pH determines the dominance of oxidant species among Cl_2 (Br_2), ClO^- (BrO^-), HOCl (HOBr) in water due to chlorination (in the presence of bromide). When disinfection and fouling control are the key issues, the availability of HOCl and HOBr in the treated water is desirable for the better outcomes. In general, at seawater pH between 7.8-8.4, the HOBr concentration is significantly available and when the pH increases (> 8.5), OCl^- and OBr^- becomes the dominant species which are less effective than HOCl or HOBr [25].

Conductivity (EC) of seawater ranged from 38.44 to 55.90 (52.63±3.48) $mScm^{-1}$. As expected, low values were registered during the NE monsoon period, and relatively higher values were observed during summer/SW monsoon. A marginal increase in EC values was observed (**Figure 4b. 3**) at the outfall discharge with values ranging from 39.16 to 56.95 (53.16±3.70) $mScm^{-1}$. A similar increase in EC values at outfall has been reported earlier [73]. DO values of seawater ranged from 4.40 to 8.40 (5.75±0.85) mg/L. The open coastal water at this location is well oxygenated due to proper mixing and phytoplankton production throughout the year [27]. A marginal decrease in DO values was observed at the outfall discharge which ranged from 3.64 to 8.40 (5.02±0.99) mg/L. The magnitude of the difference of DO contents between the intake and outfall ranged from 0.12-2.26 with an average of 0.86 mg/L. The reduction in DO content at the outfall could be attributed to its consumption during respiration of organisms residing throughout the CWS. Moreover, the difference in DO concentration between intake and outfall also could be due to the enhanced consumption of DO by the fouling organisms increased with increasing flow rate [74]. Life-sustaining activities such as respiration, feeding, metabolism, and excretion of the biofoulers settled inside the tunnel significantly affects the chemical and biological character of the cooling water [45]. In general, the addition of suspended matter to the intake water as it passed through the tunnel resulting in an increase in turbidity, reduction in the phytoplankton density leading to decrease in chlorophyll-a concentration, consumption of DO and excretion of nitrogenous wastes leading to the increase in the nutrient levels, have been reported [73]. These alterations in water quality significantly affect the chlorination chemistry and dynamics of CBP formation.

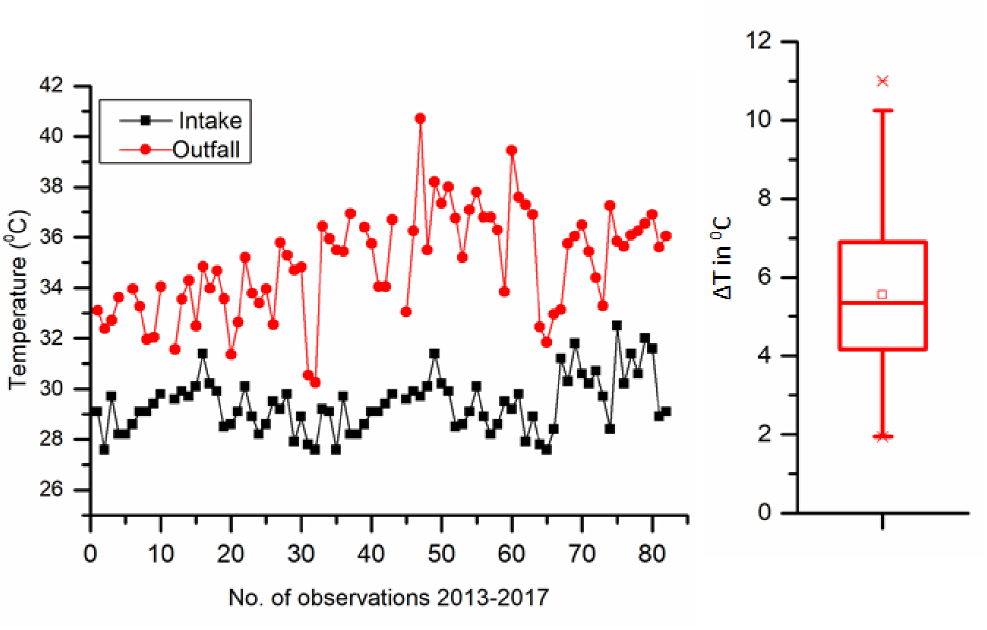


Figure 4b. 1 Variations in temperature difference between intake and discharge seawater (after extracting waste heat) of MAPS, Kalpakkam, India during 2013-2017

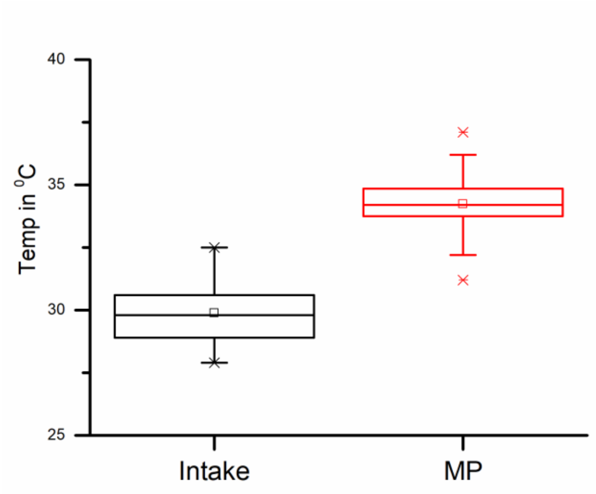


Figure 4b. 2 Summary of seawater temperature at intake and mixing point of MAPS, Kalpakkam, India during 2013-2017

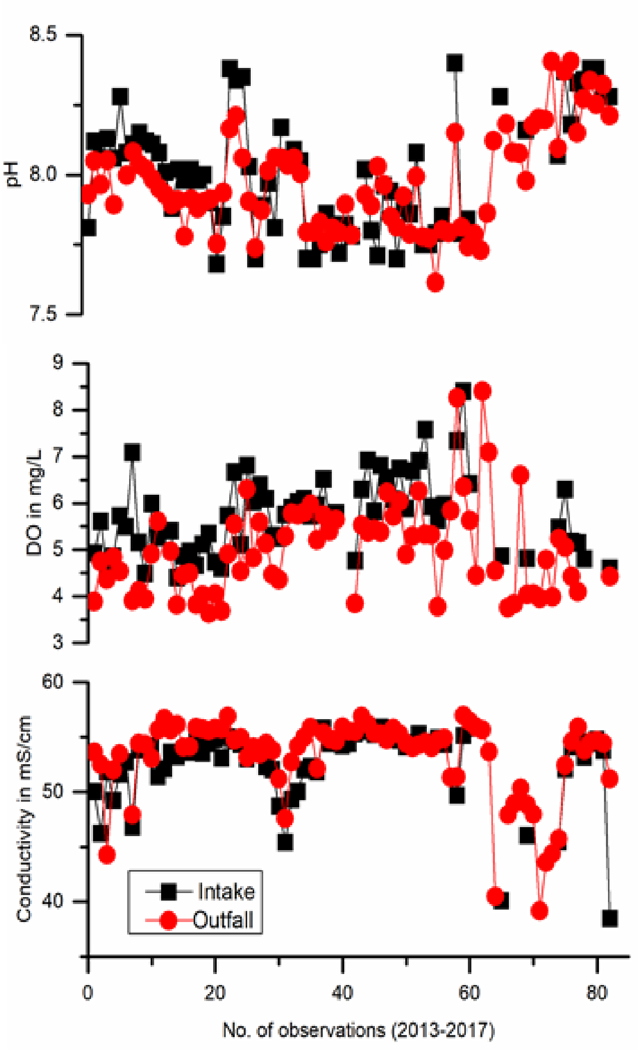


Figure 4b. 3 Variations in pH, dissolved oxygen and conductivity of seawater during 2013-2017 before (sample collected at the intake) and after passing through the condenser circuit (sample collected at outfall) of MAPS, Kalpakkam, India

4b.2.2 FRC and TRC content in the cooling water

The free residual chlorine (FRC) and total residual chlorine (TRC) contents are dependent on various factors such as chlorine dose, reaction time, temperature, ammonia concentration, and dissolved organic content. Chlorine is consumed through fast reactions with reducing inorganic compounds such as S^-, Fe^{++}, NO_2^- and gets itself reduced to chloride. It also reacts with organic matter to form chloro-organic compounds and also can oxidize them, converting to higher oxidation level compound or decomposed into CO_2 and H_2O. Chlorine consumed by these undesired reactions is generally referred to as chlorine demand (CD) of the water and is not available for biocidal action [75]. Further, the ammonia and amines present in water react with the chlorine and form the chloramines which are known as combined chlorine. Although, the combined chlorines have some biocidal action, however, the magnitude is significantly lower than that of free chlorine. The combination of FRC species such as HOCl, OCl^-, HOBr, and OBr^- and combined residual chlorine (CRC) species such as NH_2Cl, NHBrCl, $NHCl_2$, $NHBr_2$, and NH_2Br and mixture of organic chloramines are referred to as TRC (or total residual oxidant (TRO) in general). Thus, to maintain a certain level of residual, all of the above processes have to be considered and examined. In this regard, it is important to mention here that, settlement of biofoulant inside a cooling system could affect the efficiency of chlorination as they produce ammonia as their excretal product [74].

The average FRC contents in the outfall discharge ranged from 0.04 to 0.41 (0.11±0.08) mg/L in the present study. The outfall discharge of MAPS has four bays, one each for process cooling seawater-I and II (PSW-I and PSW II) and condenser cooling seawater-I and II (CSW-I and CSW-II). The discharge seawater travels through an artificial canal of about 800 m before meeting the sea at mixing point (MP). Samples were collected from the four bays at outfall and MP during the study period. The average FRC values for the four individual outlets of PSW-I, PSW-II, CSW-I, and CSW-II were 0.11, 0.13, 0.09, 0.12 mg/L respectively (**Figure 4b. 4**). A marginal reduction in FRC was observed in the CSW outlets as compared to the respective PSW outlets. The reduction could be attributed to the consumption of chlorine at an enhanced rate at a relatively high temperature in the CSW as compared to that of PSW. The TRC contents in the discharged seawater at outfall ranged from 0.06 to 0.42 (0.16±0.08) mg/L. Average values for individual outlets were 0.16, 0.18, 0.14, 0.17 mg/L for PSW-I, PSW-II, CSW-I, and CSW-II respectively. The trend observed for FRC was also similar to that of TRC in respective outlets. The contribution of combined chlorine to TRC was about 2.22 to 69.35% (32.99±17.15) during the present study. This was mostly due to the excretory ammonia produced by the biofouling organism residing inside the pre-condenser tunnel [73] leading to the formation of chlora(broma)mines such as NH_2Cl, NHClBr, $NHBr_2$, etc. due to the spontaneous reaction of chlorine with ammonia [76]. A comparison of FRC and TRC contents between the outfall discharge and mixing point samples showed a reduction in both the residuals at the mixing point (**Figure 4b. 5**). The average values for FRC and TRC at mixing point were 0.07 and 0.13 mg/L respectively. The magnitude of reduction was about 25% for FRC and 8% for TRC at the mixing point as compared to the values obtained at the outfall discharge. Thus, having a cooling canal offer double benefits such as reduction in biocide residual and decrease in the temperature before ultimately mixing into the sea. This might be due to subsequent loss of residual chlorine by several mechanisms such as volatilization, decomposition, chemical reduction during the transport along the open canal. Though in traces, residual chlorine eventually released to sea will ultimately contribute to the overall halogenated by-product formation. In some instances, where dilution and dispersion of discharge water are greatly constrained it can have a significant influence on the ambient seawater [56]. Thus, optimization of the use of chlorine following an adequate dosage regime and regular control of the residual chlorine should be part of any control strategy to limit organo-halogenated by-products formation. To maintain a particular residual at the outlet of the cooling water throughout the year, a variable dose based on the input water quality and relevant operational parameters can be adopted rather than a constant one which is generally practiced.

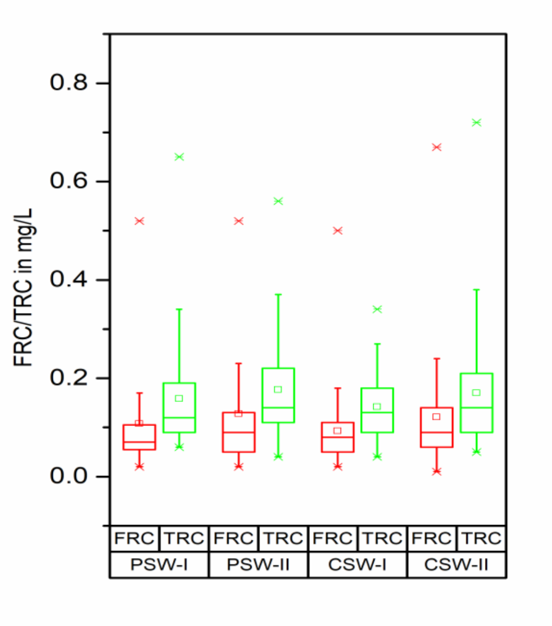


Figure 4b. 4 Magnitude of free residual chlorine (FRC) and total residual chlorine (TRC) measured at four different discharge seawater outlets (process cooling seawater- I and II (PSW-I and II), condenser cooling seawater- I and II (CSW-I& II)

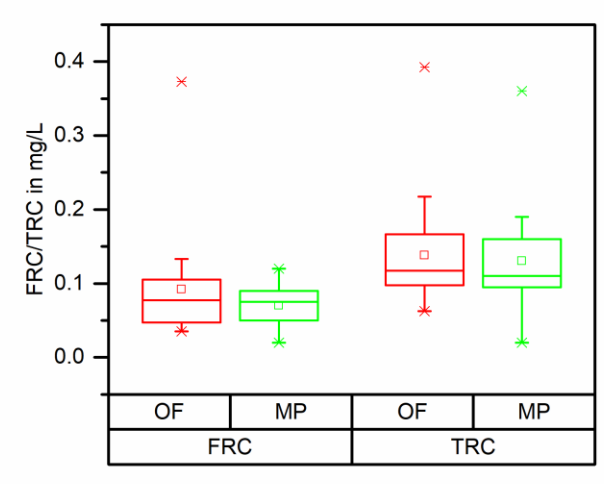


Figure 4b. 5 The difference in free residual chlorine (FRC) and total residual chlorine (TRC) content between at discharge point (outfall: OF) and mixing point (MP)

4b.2.3 Load and distribution of THMs species in the discharge water

Several parameters such as contact time, chlorine demand, temperature, pH, the concentration of precursors and bromide content influence the formation of THMs qualitatively as well as quantitatively. At the alkaline seawater pH of around 8, HOBr happens to the strongest and abundant oxidizing species, which contributes to the preferential formation of brominated by-products. When chlorine is added to seawater, active chlorine rapidly oxidizes bromide into hypobromous acid (HOBr) and hypobromite ion, those species existing in equilibrium analogous to the one between HOCl and ClO^- As a result, a mixture of four oxidative species - HOCl, HOBr, BrO^-, and ClO^- co-exist during the chlorination of bromide-rich water such as seawater. The resultant oxidants species react with the natural organic matters (NOM) present in the water via oxidation and substitution reactions. Incomplete oxidation and substitution reactions at various functional sites of NOMs, particularly at carbonyl, phenol, acetyl, carboxyl, alcohol, results in a variety of organo-halogenated by-products.

As expected, Bromoform (TBM) was the highest contributing THM constituent formed during the seawater chlorination at MAPS, Kalpakkam. It ranged from BDL to 51.42 (9.29±11.76) µg/L in the present study (**Figure 4b. 6**). TBM was the dominant fraction in almost 70% of the samples analyzed (**Figure 4b. 7**), and its average contribution to total trihalomethanes (TTHMs) was about 70.65±25.77% (range:7.49-100%) (**Figure 4b. 8**). Strong positive correlations (**Table 4b. 1**) between TBM and TTHM observed further supported the above observation. Many similar seawater chlorination studies have also reported the dominance of TBM among the THMs formed [9,10]. The contribution of chloroform (TCM) to TTHM was the second highest, and it ranged from BDL to 14.18 (2.43±2.78) µg/L. Average values of the other two fractions DBCM and BDCM were 0.42 and 0.63 µg/L respectively. A similar percentage contribution of the THMs has been reported during seawater chlorination from Arabian Gulf [77]. At a typical chlorination condition of 1 mg/L, chloroform generally does not get formed to a detectable level during seawater chlorination as observed in laboratory experiments [9]. During the actual chlorination in the nuclear power plant, chlorine gas is pre-mixed with the seawater at a very high concentration resulting in much higher Cl_2/Br^- ratio. Under this condition, depending on the period until it gets mixed with seawater at intake, large quantities of HOCl compared to HOBr become available. During this time interval formation of chloroform is favored in the chlorinated seawater and the same get reflected in the discharge water after passing through condenser conduit. TTHM values in the present study ranged from 0.04 to 65.03 (13.06±14.38) µg/L. All the values recorded were within the WHO stipulated limit of 300, 60, 100, and 100 µg/L of TCM, BDCM, DBCM, and TBM respectively with the sum of the ratio of the concentration of each to its respective guideline value not exceeding one [78]. Therefore, the present regime of low-dose continuous chlorination adopted at MAPS seawater cooling system for biofouling control is a well-designed regime with respect to meeting environmental stipulations. In the present scenario, though all the TTHM values were not very high, if a series of nuclear reactors are planned along this coast, the pressure on the coastal ecosystem with respect to CBPs flux will increase. A comparison of TTHM contents between the THMs value observed after five-day incubation to that in the discharge water showed that a significant decrease in TTHM values had occurred over time. The reduction pattern was similar for all the individual outlets of PSW and CSW (**Figure 4b. 6**). The overall average of TTHM content in the discharge water and after five days were 13.46 µg/L and 10.33 µg/L respectively. An increase in TTHM concentration was expected in the five days incubated samples due to the prolonged reaction of residual chlorine with the NOM present. However, a substantial reduction in TTHMs level was observed after five days of incubation as compared to the corresponding samples quenched immediately after collection. This could be attributed to the degradation of the THMs after reaching limiting THMs values during the five-day long incubation. Under the alkaline condition, reduction of bromo-THMs such as TBM occurred due to hydrolysis and facilitated at the higher temperature [41]. Similar processes might have caused the degradation of THMs during incubation. The above observation was supported by the fact that, a positive correlation between TTHM at the outfall and temperature was observed (**Table 4b. 1**) whereas, the correlation between TTHM of fifth day and temperature was insignificant. Formation of THMs observed to be much slower after a rapid initial formation [77], and the effect of various processes responsible for THMs reduction outweigh the magnitude of the formation during incubation. Numerous marine and terrestrial organisms also generate a variety of CBPs as part of their natural defense mechanisms. Benthic and planktonic algae were known to produce bromoform, other trihalomethanes, and bromophenols in seawater [79,80]. Although the concentration of the endogenous production of these organic substances is much lesser compared to that in disinfected discharge water, they need to be assessed to arrive at the discharge effect base-line.

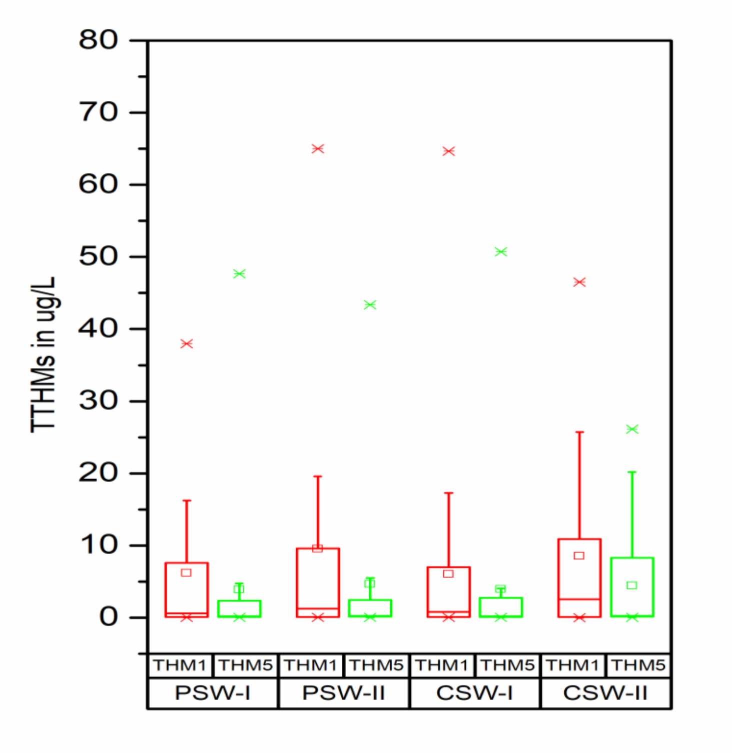


Figure 4b. 6 Comparison of trihalomethanes content at four different discharge seawater outlets (process cooling seawater-I and II (PSW-I and II), condenser cooling seawater- I and II (CSW-I and II) measured immediately (THM1) and after 5-day room temperature incubation (THM5).

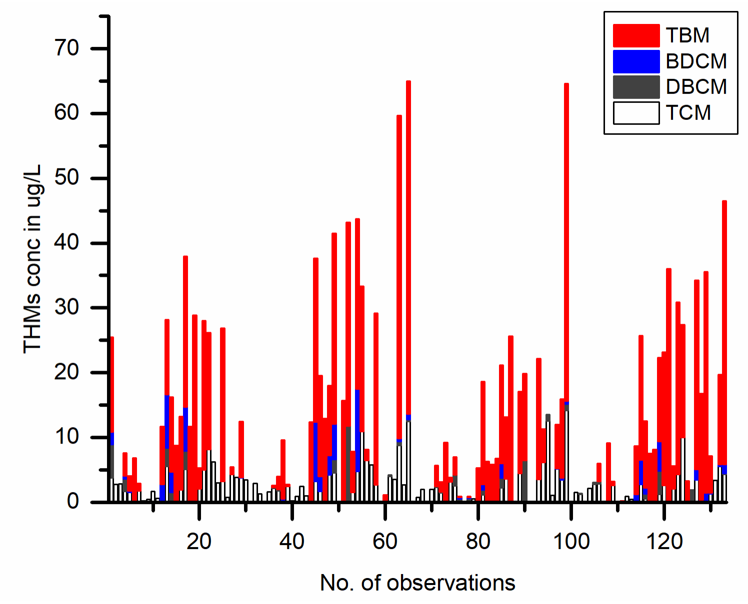


Figure 4b. 7 Distribution of four THMs species in the discharge water collected at the outfall of MAPS, Kalpakkam, India during 2013-2017.

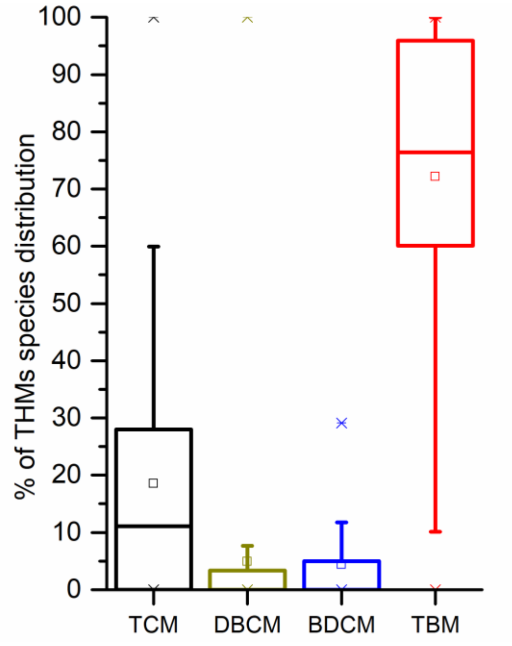


Figure 4b. 8 Overall summary (for the period 2013-2018) of percentage distribution of different THMs species to the total THM concentration in the discharge seawater due to the chlorination.

4b.2.4 Analysis of Correlation matrix

Positive correlations (**Table 4b. 1**) were observed between pH and residuals (FRC and TRC). Increase in pH shifts the HOBr ↔ OBr^- equilibrium towards the right in seawater. OBr^- is consumed less effectively compared to HOBr because of its lower reactivity. Though this had resulted in the +ve correlation of pH with TRC, this may not be an important operational consideration when seawater is used. FRC, as well as TRC, showed positive correlations with THMs content in the discharged seawater. Hung et al. (2017) [81] had found pH to have a strong effect on THM formation. In our study, pH had shown a positive correlation with THMs discharge at outfall which supports the finding of increased THMs on increasing pH by Hansen et al. (2012) [82]. Low level of THMs formation on lowering the pH was reported in different studies [83,84].

Table 4b. 1 Pearson correlation matrix of various parameters of the discharge cooling seawater of MAPS, Kalpakkam, India

	pH	Cond	DO	Temp	FRC	TRC	TCM1	DBCM1	BDCM1	TBM1	TTHM1	TCM5	DBCM5	BDCM5	TBM5	TTHM5
pH	**1**															
Cond	**-0.685**	**1**														
DO	**-0.460**	**0.599**	**1**													
Temp	-0.031	0.080	**-0.162**	**1**												
FRC	**0.250**	**-0.331**	**-0.311**	0.113	**1**											
TRC	**0.279**	**-0.347**	**-0.289**	0.031	**0.910**	**1**										
TCM1	**0.331**	**-0.399**	**-0.382**	-0.055	**0.211**	**0.238**	**1**									
DBCM1	0.018	-0.120	**-0.163**	0.037	**0.215**	**0.225**	-0.018	**1**								
BDCM1	-0.122	-0.040	-0.073	-0.013	**0.249**	**0.254**	0.124	**0.204**	**1**							
TBM1	**0.178**	**-0.319**	**-0.291**	**0.230**	**0.539**	**0.482**	**0.335**	**0.241**	**0.347**	**1**						
TTHM1	**0.203**	**-0.359**	**-0.355**	**0.182**	**0.543**	**0.501**	**0.492**	**0.322**	**0.456**	**0.967**	**1**					
TCM5	0.135	-0.032	-0.069	0.044	0.026	0.032	**0.139**	0.070	0.083	0.026	0.064	**1**				
DBCM5	0.035	0.056	-0.024	0.051	-0.025	-0.020	0.049	0.022	0.010	0.000	0.012	**0.952**	**1**			
BDCM5	0.028	-0.020	-0.071	0.084	0.008	0.018	0.132	0.046	0.128	0.068	0.101	**0.779**	**0.824**	**1**		
TBM5	-0.047	-0.114	-0.006	**0.147**	**0.268**	**0.258**	0.096	**0.149**	**0.526**	**0.402**	**0.425**	**0.221**	**0.204**	**0.416**	**1**	
TTHM5	0.036	-0.030	-0.048	0.102	0.086	0.089	0.121	0.087	**0.233**	**0.158**	**0.188**	**0.884**	**0.899**	**0.921**	**0.579**	**1**

Values in bold are significantly different from 0 with a significance level alpha=0.1, TCM1(5), DBCM1(5), BDCM1(5) and TBM1(5) represents the corresponding values measured on the same day after the quenching of residual chlorine in-situ (after five-day incubation of the unquenched samples)

However, pH control is suggested to have lesser importance in controlling brominated CBPs than chlorinated CBPs as in case of seawater chlorination [85]. The negative correlation of conductivity with THM was because of enhanced formation of THMs because of the additional organic input through runoff while reducing the conductivity of seawater during monsoon due to the freshwater flux to the sea. Similarly, DO also exhibited a negative correlation with THMs in the discharge water. Low values of dissolved oxygen are often to indicate the presence of biological and detrital matter [86]. Moreover, dissolved oxygen consumption and production are influenced by plant and algal biomass, light intensity and water temperature, and are subject to diurnal and seasonal variations [87]. All these parameters affect the chlorine reactivity and thereby the formation of THMs. As expected, the temperature was positively correlated with the THMs discharge. In general, temperature enhances the rate of reaction; however, the effect of temperature on the load of THMs was the resultant effect of formation and decomposition. THM reduction, especially brominated THMs, due to hydrolysis at elevated temperature was also reported by [41].

4b.3 Conclusion

TRC level of 0.13 mg/L (average during 2013-2017) in the discharge seawater will further get reduced by several mechanisms such as dilution, volatilization, decomposition leaving only a trace beyond the mixing zone. The TRC values were within the pollution control board stipulated value of 0.5 mg/L. The average values for FRC and TRC at mixing point were 0.07 and 0.13 mg/L respectively. The magnitude of reduction was about 25% for FRC and 8% for TRC at the mixing point as compared to the values obtained at the outfall discharge. TTHM values in the present study ranged from 0.04 to 65.03 (13.06±14.38) µg/L which is much below the WHO 2011 guideline values. A few more nuclear reactors are being planned along this coast. Thus, the resultant increase in the burden on the coastal ecosystem with respect to CBPs has to be evaluated in detail taking the fate and transport of different CBPs class into account. Water quality parameters such as DO, temperature, pH have shown to affect both residual chlorine and trihalomethanes content in the discharge seawater effluents. The present low dose chlorination adopted at MAPS seawater cooling system not only serves the operational requirement of biofouling control but also helps to comply with the environmental restriction of Cl_2 residual and trihalomethanes.

References

[1] M.P. Abdullah, L.F. Yee, S. Ata, A. Abdullah, B. Ishak, K.N.Z. Abidin, The study of interrelationship between raw water quality parameters, chlorine demand and the formation of disinfection by-products, Phys. Chem. Earth. 34 (2009) 806–811.

[2] H. Gallard, U. Von Gunten, Chlorination of natural organic matter: Kinetics of chlorination and of THM formation, Water Res. 36 (2002) 65–74.

[3] D. Ristoiu, U. von Gunten, A. Mocan, R. Chira, B. Siegfried, M. Haydee Kovacs, S. Vancea, Trihalomethane formation during water disinfection in four water supplies in the Somes river basin in Romania., Environ. Sci. Pollut. Res. Int. 16 Suppl 1 (2009) S55–S65.

[4] M. Ahmadi, B. Ramavandi, The formation potential of haloacetonitriles in the dez river water, Iran, Environ. Technol. (United Kingdom). 35 (2014) 2347–2355.

[5] M. Fooladvand, B. Ramavandi, K. Zandi, M. Ardestani, Investigation of trihalomethanes formation potential in Karoon River water, Iran, Environ. Monit. Assess. 178 (2011) 63–71.

[6] A.D. Nikolaou, S.K. Golfinopoulos, T.D. Lekkas, M.N. Kostopoulou, DBP levels in chlorinated drinking water: Effect of humic substances, Environ. Monit. Assess. 93 (2004) 301–319.

[7] B. Ye, W. Wang, L. Yang, J. Wei, Factors influencing disinfection by-products formation in drinking water of six cities in China, J. Hazard. Mater. 171 (2009) 147–152.

[8] US EPA, Integrated Risk Information System (IRIS) Database for Risk Assessment, (2007).

[9] R.K. Padhi, M. Sowmya, A.K. Mohanty, S.N. Bramha, K.K. Satpathy, Formation and speciation characteristics of brominated trihalomethanes in seawater chlorination, Water Environ. Res. 84 (2012) 2003–2009.

[10] M. Fabbricino, G. V. Korshin, Formation of disinfection by-products and applicability of differential absorbance spectroscopy to monitor halogenation in chlorinated coastal and deep ocean seawater, Desalination. 176 (2005) 57–69.

[11] H.A. Jenner, C.J.L. Taylor, M. Van Donk, M. Khalanski, Chlorination by-products in chlorinated cooling water of some European coastal power stations, Mar. Environ. Res. 43 (1997) 279–293.

[12] E. Agus, N. Voutchkov, D.L. Sedlak, Disinfection by-products and their potential impact on the quality of water produced by desalination systems: A literature review, Desalination. 237 (2009) 214–237.

[13] D.M. Golea, A. Upton, P. Jarvis, G. Moore, S. Sutherland, S.A. Parsons, S.J. Judd, THM and HAA formation from NOM in raw and treated surface waters, Water Res. 112 (2017) 226–235.

[14] J.C. Lou, C.E. Huang, J.Y. Han, Y.J. Huang, Generation of disinfection by-products (DBPs) at two advanced water treatment plants, Environ. Monit. Assess. 162 (2010) 365–375.

[15] N.P. Thacker, V. Nitnaware, Factors influencing formation of trihalomethanes in swimming pool water, Bull. Environ. Contam. Toxicol. 71 (2003) 633–640.

[16] S. Chowdhury, K. Alhooshani, T. Karanfil, Disinfection byproducts in swimming pool: Occurrences, implications and future needs, Water Res. 53 (2014) 68–109.

[17] T. Manasfi, M. De Méo, B. Coulomb, C. Di Giorgio, J.-L. Boudenne, Identification of disinfection by-products in freshwater and seawater swimming pools and evaluation of genotoxicity, Environ. Int. 88 (2016) 94–102.

[18] R. Xue, H. Shi, Y. Ma, J. Yang, B. Hua, E.C. Inniss, C.D. Adams, T. Eichholz, Evaluation of thirteen haloacetic acids and ten trihalomethanes formation by peracetic acid and chlorine drinking water disinfection, Chemosphere. 189 (2017) 349–356.

[19] J. Wang, Z. Hao, F. Shi, Y. Yin, D. Cao, Z. Yao, J. Liu, Characterization of Brominated Disinfection Byproducts Formed during the Chlorination of Aquaculture Seawater, Environ. Sci. Technol. 52 (2018) 5662–5670.

[20] J. Deng, C. Liu, L. Yu, B. Zhou, Chronic exposure to environmental levels of tribromophenol impairs zebrafish reproduction, Toxicol. Appl. Pharmacol. 243 (2009) 87–95.

[21] J. Parinet, S. Tabaries, B. Coulomb, L. Vassalo, J.-L. Boudenne, Exposure levels to brominated compounds in seawater swimming pools treated with chlorine, Water Res. 46 (2012) 828–836.

[22] B. Ramavandi, S. Farjadfard, M. Ardjmand, S. Dobaradaran, Effect of water quality and operational parameters on trihalomethanes formation potential in Dez River water, Iran, Water Resour. Ind. 11 (2015) 1–12.

[23] A.K. Mohanty, K.K. Satpathy, M.V.R. Prasad, Changes in sub-soil river water quality upon its open storage—a case study, Environ. Monit. Assess. 189 (2017) 399.

[24] R.K. Padhi, K.K. Satpathy, S. Subramanian, Impact of groundwater surface storage on chlorination and disinfection by-product formation, J. Water Health. 13 (2015) 838.

[25] A.G.I. Dalvi, R. Al-Rasheed, M.A. Javeed, Haloacetic acids (HAAs) formation in desalination processes from disinfectants, Desalination. 129 (2000) 261–271.

[26] K.K. Satpathy, K.V.K. Nair, P.K. Mathur, Chlorine demand & chemical control of biofouling in power plant cooling system, in: M.P. Thompson, R. Nagabhushanam (Eds.), Recent Dev. Biofouling Control, Oxford Oxford & IBH Publishing Company, New Delhi, 1994: pp. 397–407.

[27] G. Sahu, K.K. Satpathy, A.K. Mohanty, S.K. Sarkar, Variations in community Structure ofPhytoplankton in Relation to Physicochemical Properties of Coastal Waters, Southeast Coast of India, Indian J. Mar. Sci. 41 (2012) 223–241.

[28] J. Garnier, G. Billen, L. Palfner, Understanding the oxygen budget and related ecological processes in the river Mosel: the RIVERSTRAHLER approach, Hydrobiologia. 410 (1999) 151–166.

[29] A.T. Chow, S. Gao, R.A. Dahlgren, Physical and chemical fractionation of dissolved organic matter and trihalomethane precursors: A review, J. Water Supply Res. Technol. - Aqua. 54 (2005).

[30] H.C. Hong, A. Mazumder, M.H. Wong, Y. Liang, Yield of trihalomethanes and haloacetic acids upon chlorinating algal cells, and its prediction via algal cellular biochemical composition, Water Res. 42 (2008) 4941–4948.

[31] J.D. Plummer, J.K. Edzwald, Effect of ozone on algae as precursors for trihalomethane and haloacetic acid production., Environ. Sci. Technol. 35 (2001) 3661–8.

[32] D.A. Reckhow, P.C. Singer, R.L. Malcolm, Chlorination of humic materials: byproduct formation and chemical interpretations, Environ. Sci. Technol. 24 (1990) 1655–1664.

[33] R. Fabris, C.W.K. Chow, M. Drikas, B. Eikebrokk, Comparison of NOM character in selected Australian and Norwegian drinking waters, Water Res. 42 (2008) 4188–4196.

[34] H. Mash, P.K. Westerhoff, L.A. Baker, R.A. Nieman, M.-L. Nguyen, Dissolved organic matter in Arizona reservoirs: assessment of carbonaceous sources, Org. Geochem. 35 (2004) 831–843.

[35] J.L. Weishaar, G.R. Aiken, B.A. Bergamaschi, M.S. Fram, Roger Fujii, K. Mopper, Evaluation of Specific Ultraviolet Absorbance as an Indicator of the Chemical Composition and Reactivity of Dissolved Organic Carbon, Environ. Sci. Technol. 37 (2003) 4702–4708.

[36] N. Ates, S.S. Kaplan, E. Sahinkaya, M. Kitis, F.B. Dilek, U. Yetis, Occurrence of disinfection by-products in low DOC surface waters in Turkey, J. Hazard. Mater. 142 (2007) 526–534.

[37] E.E.E. Chang, Y.P.P. Lin, P.C.C. Chiang, Effects of bromide on the formation of THMs and HAAs, Chemosphere. 43 (2001) 1029–1034.

[38] G. Hua, D.A. Reckhow, J. Kim, Effect of Bromide and Iodide Ions on the Formation and Speciation of Disinfection Byproducts during Chlorination, Environ. Sci. Technol. Technol. 40 (2006) 3050–3056.

[39] F. Sun, J. Chen, Q. Tong, S. Zeng, Development and identification of an integrated waterworks model for trihalomethanes simulation, Sci. Total Environ. 407 (2009) 2077–2086.

[40] T. Bond, N.H. Mokhtar Kamal, T. Bonnisseau, M.R. Templeton, Disinfection by-product formation from the chlorination and chloramination of amines, J. Hazard. Mater. 278 (2014) 288–296.

[41] X. lu Zhang, H. wei Yang, X. mao Wang, T. Karanfil, Y.F. Xie, Trihalomethane hydrolysis in drinking water at elevated temperatures, Water Res. 78 (2015) 18–27.

[42] G. Hua, D.A. Reckhow, Evaluation of bromine substitution factors of DBPs during chlorination and chloramination, Water Res. 46 (2012) 4208–4216.

[43] H. Hong, L. Qian, Y. Xiong, Z. Xiao, H. Lin, H. Yu, Use of multiple regression models to evaluate the formation of halonitromethane via chlorination/chloramination of water from Tai Lake and the Qiantang River, China, Chemosphere. 119 (2015) 540–546.

[44] M. Al-Bloushi, J. Saththasivam, S. Jeong, G.L. Amy, T.O. Leiknes, Effect of organic on chemical oxidation for biofouling control in pilot-scale seawater cooling towers, J. Water Process Eng. 20 (2017) 1–7.

[45] J.G. Masilamoni, K.S. Jesudoss, K. Nandakumar, K.K. Satpathy, K.V.K. Nair, J. Azariah, Jellyfish ingress: A threat to the smooth operation of coastal power plants, Curr. Sci. 79 (2000) 567–569.

[46] K.K. Satpathy, A.K. Mohanty, G. Sahu, S.K. Sarkar, U. Natesan, R. Venkatesan, M.V.R. Prasad, Variations of physicochemical properties in Kalpakkam coastal waters, east coast of India, during southwest to northeast monsoon transition period, Environ. Monit. Assess. 171 (2010) 411–424.

[47] K.V.K. Nair, Marine biofouling and its control with particular reference to condenser-cooling circuits of power plants - an overview, J. Indian Inst. Sci. 79 (1999) 497–511.

[48] E.H. Poornima, M. Rajadurai, V.N.R. Rao, S.V. Narasimhan, V.P. Venugopalan, Use of coastal waters as condenser coolant in electric power plants: Impact on phytoplankton and primary productivity, J. Therm. Biol. 31 (2006) 556–564.

[49] N. Saravanane, K.K. Satpathy, K.V.K. Nair, G. Durairaj, Preliminary observations on the recovery of tropical phytoplankton after entrainment, J. Therm. Biol. 23 (1998) 91–97.

[50] V. Ebenezer, Y.V. Nancharaiah, V.P. Venugopalan, Chlorination-induced cellular damage and recovery in marine microalga, Chlorella salina, Chemosphere. 89 (2012) 1042–1047.

[51] P. Chavan, R. Kumar, R. Kirubagaran, V.P. Venugopalan, Comparative toxicological effects of two antifouling biocides on the marine diatom Chaetoceros lorenzianus: Damage and post-exposure recovery, Ecotoxicol. Environ. Saf. 144 (2017) 97–106.

[52] M.J. Plewa, Y. Kargalioglu, D. Vankerk, R.A. Minear, E.D. Wagner, Mammalian cell cytotoxicity and genotoxicity analysis of drinking water disinfection by-products, Environ. Mol. Mutagen. 40 (2002) 134–142.

[53] Y. Pan, X. Zhang, Y. Li, Identification, toxicity and control of iodinated disinfection byproducts in cooking with simulated chlor(am)inated tap water and iodized table salt, Water Res. 88 (2016) 60–68.

[54] D. Boudjellaba, J. Dron, G. Revenko, C. D??melas, J.L. Boudenne, Chlorination by-product concentration levels in seawater and fish of an industrialised bay (Gulf of Fos, France) exposed to multiple chlorinated effluents, Sci. Total Environ. 541 (2016) 391–399.

[55] M. Khalanski, H.A. Jenner, Chlorination chemistry and ecotoxicology of the marine cooling water systems, in: Oper. Environ. Consequences Large Ind. Cool. Water Syst., Springer US, Boston, MA, 2012: pp. 183–226.

[56] C.J.L.L. Taylor, The effects of biological fouling control at coastal and estuarine power stations, Mar. Pollut. Bull. 53 (2006) 30–48.

[57] E. Agus, D.L. Sedlak, Formation and fate of chlorination by-products in reverse osmosis desalination systems, Water Res. 44 (2010) 1616–1626.

[58] R. Rajamohan, E. Vinnitha, V.P. Venugopalan, S. V. Narasimhan, Chlorination by-products and their discharge from the cooling water system of a coastal electric plant, Curr. Sci. 93 (2007) 1608–1612.

[59] K.K. Satpathy, S.D. Ruth Nithila, Chlorination for biofouling control in power plant cooling water system - a review, (2008).

[60] K.K. Satpathy, K.V.K. Nair, Impact of power plant discharge on the physico-chemical characteristics of Kalpakkam coastal waters, Mahasagar – Bull. Natl. Inst. Oceanogr. 23 (1990) 117–125.

[61] G. Brankevich, R. Bastida, C. Lemmi, A comparative study of biofouling settlements in different sections of necochea power plant (quequen port, Argentina), Biofouling. 1 (1988) 113–135.

[62] N. Sasikurnar, S. Rajagopal, K. V K Nair, Seasonal and vertical distribution of macrofoulants in Kalpakkam coastal waters, 1989.

[63] P. Balamurugan, M. Hiren Joshi, T.S. Rao, Microbial fouling community analysis of the cooling water system of a nuclear test reactor with emphasis on sulphate reducing bacteria, Biofouling. 27 (2011) 967–978.

[64] P. Rajala, E. Sohlberg, O. Priha, I. Tsitko, H. Väisänen, M. Tausa, L. Carpén, P. Rajala, E. Sohlberg, O. Priha, I. Tsitko, H. Väisänen, M. Tausa, L. Carpén, Biofouling on Coated Carbon Steel in Cooling Water Cycles Using Brackish Seawater, J. Mar. Sci. Eng. 4 (2016) 74.

[65] V.P. Venugopalan, K.V.K. Nair, Effect of biofouling community on cooling water characteristics of a coastal power plant, Indian J. Mar. Sci. 19 (1990) 294–296.

[66] K.K. Satpathy, K.V.K. Nair, P.K. Mathur, Chlorine demand & chemical control of biofouling in power plant cooling system, in: M.P. Thompson, R. Nagabhushanam (Eds.), Recent Dev. Biofouling Control, Oxford & IBH Publish, 1994: pp. 397–407.

[67] K.K. Satpathy, V.P. Venugopalan, K.V.K. Nair, Barnacle fouling control technology in power plant cooling system, in: M.P. Thompson, R. Nagbhushanam (Eds.), Barnacle Fouling Ecophysiol. Control Technol., American Institute of Biological Sciences, Washington D.C., 1999: pp. 359–379.

[68] N. Sasikurnar, Ecology and control of biofouling in a coastal power station with special reference to Megabalanus tintinabulum (L), University of Madras Madras, India, 1991.

[69] S. Rajagopal, N. Sasikumar, J. Azariah, K.V.K. Nair, Some observations on biofouling in the cooling water conduits of a coastal power plant, Biofouling. 3 (1991) 311–324.

[70] K.V.K. Nair, Biofouling porblems in cooling conduits of power stations, in: Adv. Aquat. Biol. Fish., 1987: pp. 257–262.

[71] K.K. Satpathy, Studies on the chemical features of cooling water systems in the context of scaling, biofouling and corrosion control, Madras University, India, 1996.

[72] I. Valiela, Marine ecological processes, Springer, 1995.

[73] K.K. Mohanty, A.K.; Prasad M.V.R.; and Satpathy, Alteration in physico-chemical properties of the cooling water by the macrofouling community in the intake tunnel of a coastal power plant, in: Proc. OPENWAC, 2008: pp. 324–328.

[74] K.K. Satpathy, Effect of biofouling on the cooling water quality of a nuclear power plant, Bull. Electrochem. (1999) 143–147.

[75] G.C. White, The handbook of chlorination, Van Nostrand Reinhold Co, 1986.

[76] R. Liu, C. Tian, C. Hu, Z. Qi, H. Liu, J. Qu, Effects of bromide on the formation and transformation of disinfection by-products during chlorination and chloramination, Sci. Total Environ. 625 (2018) 252–261.

[77] A. Abdel-Wahab, Formation of Trihalomethanes during Seawater Chlorination, J. Environ. Prot. (Irvine,. Calif). 01 (2010) 456–465.

[78] WHO, WHO guidelines for drinking-water quality-4th edition, 2011.

[79] I. Stemmler, I. Hense, B. Quack, Marine sources of bromoform in the global open ocean-global patterns and emissions, Biogeosciences. 12 (2015) 1967–1981.

[80] V.P. Venugopalan, S. Rajagopal, H.A. Jenner, Operational and Environmental Issues Relating to Industrial Cooling Water Systems: An Overview, in: Oper. Environ. Consequences Large Ind. Cool. Water Syst., Springer US, Boston, MA, 2012: pp. 1–12.

[81] Y.-C. Hung, B.W. Waters, V.K. Yemmireddy, C.-H. Huang, pH effect on the formation of THM and HAA disinfection byproducts and potential control strategies for food processing, J. Integr. Agric. 16 (2017) 2914–2923.

[82] K.M.S. Hansen, S. Willach, M.G. Antoniou, H. Mosbæk, H.-J. Albrechtsen, H.R. Andersen, Effect of pH on the formation of disinfection byproducts in swimming pool water - Is less THM better?, Water Res. 46 (2012) 6399–409.

[83] S.K. Golfinopoulos, G.B. Arhonditsis, Quantitative assessment of trihalomethane formation using simulations of reaction kinetics, Water Res. 36 (2002) 2856–2868.

[84] A.D. Nikolaou, S.K. Golfinopoulos, T.D. Lekkas, G.B. Arhonditsis, Factors affecting the formation of organic by-products during water chlorination: A bench-scale study, Water. Air. Soil Pollut. 159 (2004) 357–371.

[85] H. Hong, X. Yan, X. Song, Y. Qin, H. Sun, H. Lin, J. Chen, Y. Liang, Bromine incorporation into five DBP classes upon chlorination of water with extremely low SUVA values, Sci. Total Environ. 590–591 (2017) 720–728.

[86] L.D. Talley, G.L. Pickard, W.J. Emery, J.H. (Oceanographer) Swift, Descriptive physical oceanography : an introduction, Academic Press, 2011.

[87] D.W. Connell, G.J. Miller, Chemistry and ecotoxicology of pollution, Wiley, 1984.

CHAPTER 5

FORMATION, KINETICS AND SPECIES DISTRIBUTION OF TRIHALOMETHANES DURING CHLORINATION

(This chapter presents various important phenomena on THMs formation in two sections; **Chapter 5a** addresses effects of various parameters on the formation, yield and speciation of four THMs species during seawater chlorination, **Chapter 5b** addresses the effect of water storage in an open reservoir on the freshwater physicochemical characters and thus on chlorination efficacy and by-products formation.)

Chapter 5a

Formation and speciation characteristics of trihalomethanes during seawater chlorination

Abstract: Formation character of brominated-trihalomethanes (Br-THMs) in chlorinated seawater and its dependence on applied chlorine dose, reaction time, and temperature were investigated in the laboratory. Seawater was collected from the jetty of Madras Atomic Power station (MAPS), southeast coast of India and a chlorine dose of 1, 3, 5, and 10 mg/L were each applied at a temperature of 20, 30, and 40 ºC to investigate the yield and kinetics of Br-THMs formation. Qualitative and quantitative estimation of THM formation at various time intervals ranging from 5 min to 168 h was determined. Chlorine dose, chlorine contact time, and reaction temperature positively affected the load of THMs. The ratio of chlorine dose to halogen incorporation decreased from 12% to 5% with increasing applied chlorine dose from 1 to 10 mg/L. Significant levels of THMs were found to be formed within 0.5 h of reaction, followed by a very slow rate of formation. Elevated temperature favored both increased rate of formation and overall THM yield. The formation order of different trihalomethane species at all studied temperatures was observed to be bromodichloromethane ($CHCl_2Br$) < dibromochloromethane ($CHClBr_2$) < bromoform ($CHBr_3$). Formation of $CHCl_3$ was not observed, and bromoform was the dominant (96% to 98%) among the three THM species formed. Short time course chlorine demand of intake seawater alone could be used to effectively predict the THM concentration with acceptable uncertainties.

5a.1 Introduction

THMs are deemed as the most ubiquitous dominant constituents of byproducts in chlorinated surface waters and have received the most attention. Chlorine undergoes addition and substitution reactions with natural organic matters (NOMs) such as humic and fulvic acids, including that of compounds such as algae, chlorophyll, proteins, amino acids, etc., forming THMs [1,2]. Chlorination of seawater differs from that of freshwater because of (1) the different biogeochemical NOM generation pathways between terrestrial and marine systems and (2) the presence of ~65 mg/L bromide as compared with the negligible amount of bromide present in freshwater [3]. Oxidation of bromide by chlorine leads to the predominant formation of brominated CBPs [4,5]. Brominated CBPs are reported to be more harmful than their chlorine analog [6] and hence need to be monitored to control their adverse effects on marine organisms when chlorinated seawater is discharged into the sea [7,8]. Moreover, volatilization of THMs with attendant effects on the atmosphere and permeation of CBPs into drinking water produced by seawater desalination is also of concern [9].

In this context, the present study factors that might influence the kinetics of formation and overall yield of CBPs in chlorinated seawater. Dependence of load and character of THM formation on chlorine dose, contact time, and the reaction temperature was investigated to evaluate its formation kinetics during seawater chlorination. Although bromide concentration and pH greatly affect the THM formation and species distribution, the variability of these two factors in seawater is practically insignificant and not feasible to control during its use by industrial water utilities.

5a.2 Results and discussion

Characteristics of the seawater taken for the investigation of the effect of temperature, chlorine dose, and contact time is summarized in **Table 5a. 1**. Chlorination experiments were carried out for 0 to 168 h of reaction time, the highest observed concentration of total trihalomethanes (TTHMs) formed at the end of 168 h ranged from 80 µg/L (for 20 ºC, 1 mg/L Cl_2 dose) to 750 µg/L (for 40 ºC, 10 mg/L Cl_2 dose). Changes in temperature, chlorine dose, and contact time of chlorination were observed to affect the overall load of THM formation significantly.

Table 5a. 1 Summary of seawater characteristic taken for investigation

Parameters	**Ranges**	**Parameters**	**Ranges**
Temp.(^{0}C)	28.5-29.3	Nitrate (µmol/L)	BDL-0.020
pH	7.9-8.1	Nitrite (µmol/L)	0.031-0.040
Salinity (psu)	30.2-31.7	Ammonia (µmol/L)	2.23-2.81
Turbidity (NTU)	1.89-2.09	TN (µmol/L)	7.62-9.34
DO (mg/L)	6.9-7.7	Phosphate (µmol/L)	0.26-0.32
TOC (mg/L)	1.69-1.88	TP (µmol/L)	0.28-0.32
Chl-a (mg/m^3)	1.01-1.05	Silicate (µmol/L)	11.25-13.3

DO: Dissolve Oxygen, TN: Total Nitrogen, TOC: Total organic Carbon, TP: Total Phosphate, Chl-a: Chlorophyll-a; BDL: Below Detection Limit

5a.2.1 Effect of temperature, Cl_2 dose, and contact time on THMs formation.

Temperature is an important factor that influences the chemical reaction kinetics, and therefore higher concentrations of CBP formation were obtained at higher temperatures. Elevated temperatures have a positive effect on CBP formation, as a result of faster formation reactions [10]. However, it must be noted that this could not be the case for all the compounds, because a temperature increase will result in not only faster formation kinetics, but also faster decomposition kinetics, as has been reported for haloacetonitriles and haloketones [11]. Higher formation kinetics of CBPs was also indicated by the rapid consumption of residual chlorine at elevated temperatures. The final concentration of CBPs is probably the result of the balance between formation and decomposition kinetics. It was observed that not only the rate of formation of THMs increased but also the total yield was higher as the temperature increased. The load of THMs increased from 80% to 90% more when the temperature was increased from 20 to 40 ºC at all applied Cl_2 doses, except for 1 0 mg/L, for which only a 35% increase was observed. This could be caused by complete exhaustion of residual chlorine for further reaction at this low Cl_2 dose. The increase in the overall yield of THM was more significant when the temperature was increased from 30 to 40 ºC, as compared with the increase in temperature from 20 to 30 ºC (**Figure 5a. 1**). This may be because some NOM fractions have become reactive at elevated temperatures that were otherwise inactive and became liable to react with the available oxidant, forming more THMs at higher temperatures. Comparatively more NOM fractions became reactive when the temperature rose above 30 ºC. These results also underline the need to further investigate CBP formation and decomposition kinetics under different ranges of conditions.

Dependence of possible load character of THMs with reaction time during the chlorination of seawater is detailed in **Figure 5a. 2**. THMs in the chlorinated seawater was found to form via a fast-initial reaction, and the trend was consistent for all the chlorine dose and temperatures studied. A significant amount of THMs was formed within a very short period of contact time, and the rate of formation was observed to be subsidized and became considerably slower after 5 h for all studied temperatures and chlorine doses (**Figure 5a. 2**). However, at the end of 5 h of reaction time, the concentration of THMs formed represented only 50% of the total yield and THMs were observed to be continuing to form even up to 168 h of reaction time at a very low rate. This indicated the existence of different reactive NOM fractions, that is, fast reactive and slow reactive fractions. The fast-reactive fraction is responsible for the initial rapid formation of THMs, whereas the slow reactive fraction results in the continual formation of THMs up to several tens of hours. The continuance of THM formation for such a long period also indicated the possible formation of THM caused by the transformation of some initially formed long-chain chlorinated organic by-products.

Chlorine dose is one of the most important factors which significantly affects the THMs formation. Higher chlorine doses favored the formation of a higher concentration of CBPs. Although a higher chlorine dose linearly favored a higher overall THM concentration (**Figure 5a. 3 (a)**), the fraction of halogen incorporation was observed to decrease gradually from 12% to 5% equivalent of the applied chlorine with increasing chlorine doses from 1 to 10 mg/L (**Figure 5a. 3 (b)**). This may be caused by the insufficient amount of the fast-reactive fraction of NOMs available to be incorporated by the chlorine residual at a higher concentration to produce a proportionate amount of initial yield. In the second stage of slower THM formation, the available chlorine also probably underwent other simultaneous competitive reactions to generate other products along with THMs. Hence, although a higher overall yield of THMs was found at higher chlorine doses, the resultant percentage of halogen incorporation decreased as the concentration of applied chlorine dose increased.

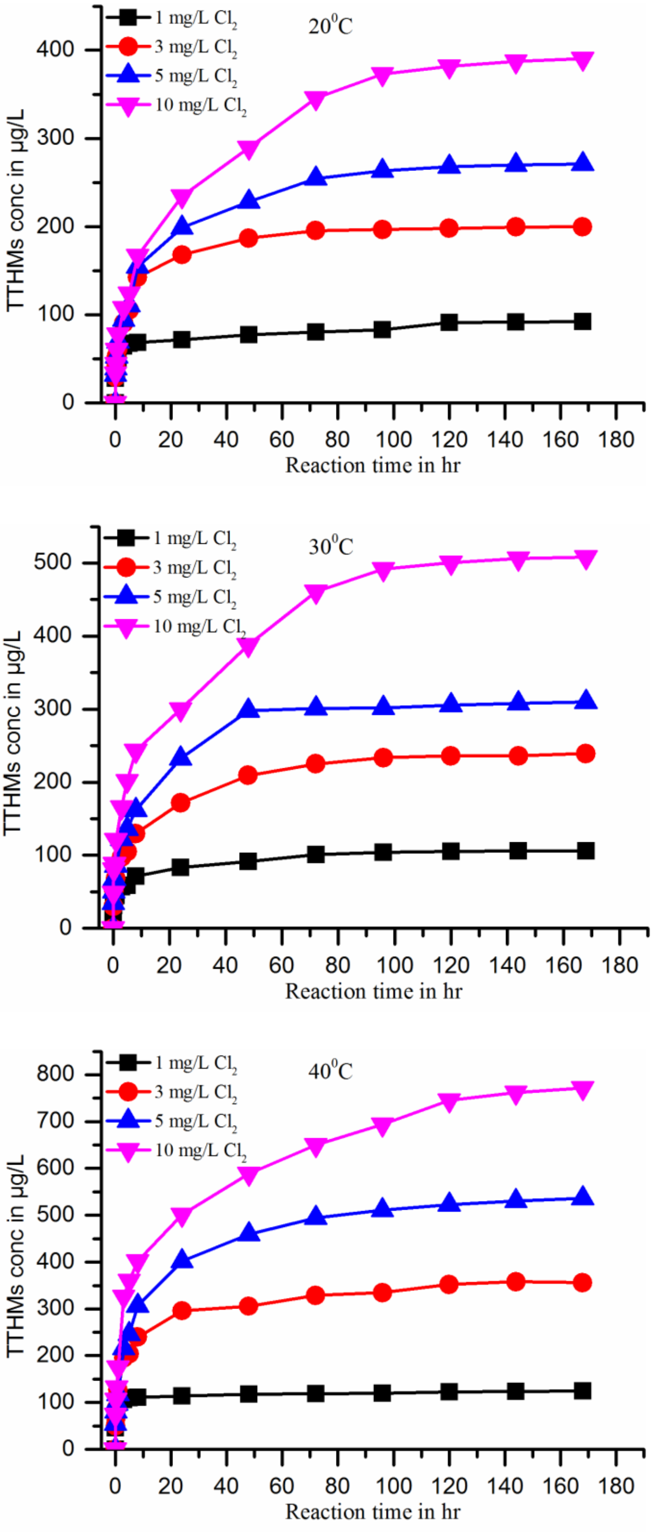


Figure 5a. 1 Time-course influence of temperatures at (a) 20 ºC, (b) 30 ºC, and (c) 40 ºC on formation characteristics and yield of THMs at various chlorine doses

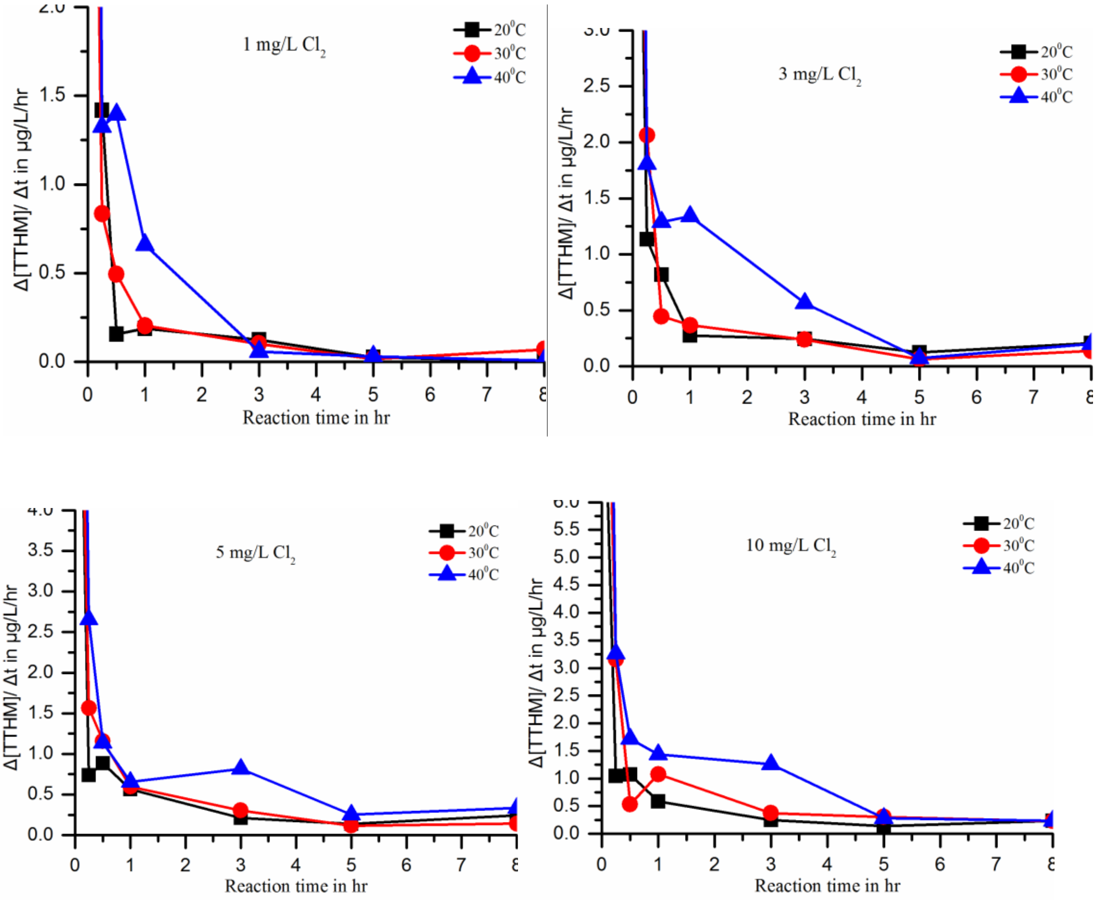


Figure 5a. 2 Short-term time course behavior of rate of THM formation (Δ [THMs]/Δt) at various Cl_2 doses and temperatures. (a): 10 mg/L (b): 5 mg/L (c): 3 mg/L (d): 1 mg/L of Cl_2

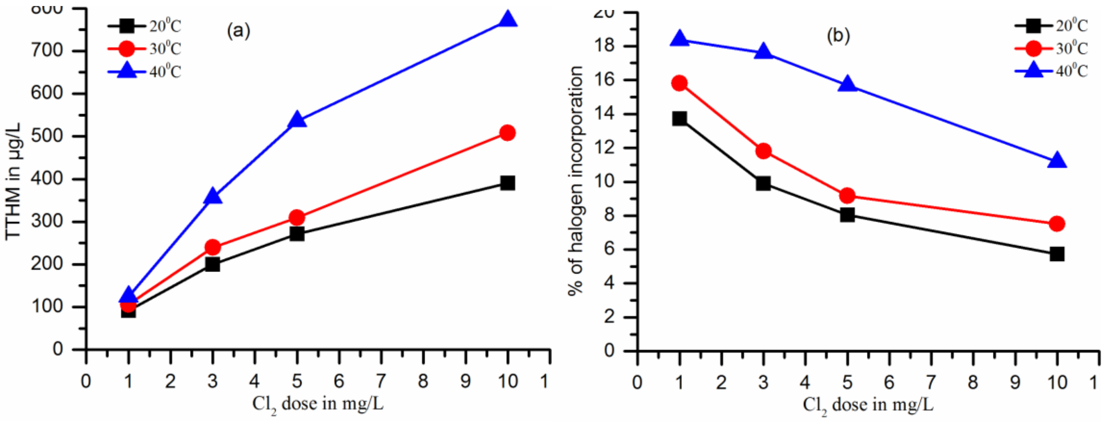


Figure 5a. 3 (a) Effect of chlorine dose on total yield of THMs (µg/L) and **(b)** correlation of halogen incorporation percentage with chlorine dose at different reaction temperatures

5a.2.2 Speciation Characteristics of THMs.

The overall formation order of THMs species at all experimental conditions was observed to be $CHCI_2Br$ < $CHClBr_2$ < $CHBr_3$, and formation of $CHCl_3$ was not observed (**Figure 5a. 4**). In agreement with the observations made by earlier reports [9,12], bromoform was observed to be the main constituent (96% to 98%) of the THMs in the chlorinated seawater under all experimental conditions. Bromoform concentration was 103.69, 228.33, 295.54, 479.22 µg/L, out of the total THMs of 91.44, 198.10, 268.18, 382.07 µg/L formed for 1, 3, 5, 10 mg/L of Cl_2 dose respectively at 30^0C and 168 h of reaction time. This could be attributed to the formation of hypobromous acid (HOBr) caused by the reaction of HOCl and Br^- in water [13]

$$\mathrm{Cl_2 + H_2O \leftrightarrow HOCl + H^- + Cl^-} \qquad (5a.1)$$

$$\mathrm{HOCl + Br^- \leftrightarrow HOBr} \qquad \mathrm{Rate_{298}} = 2.95 * 10^3 \mathrm{s^{-1}} \qquad (5a.2)$$

Reaction (5a.2) is fast enough to make a 99% conversion of HOCl to HOBr in typical seawater of salinity 35 PSU in about 10 s [14]. Because of the presence of a sufficient amount of bromide ion (65 mg/L) and the fast conversion of HOCl to HOBr, there is hardly any HOCl molecule that coexists with HOBr in seawater chlorination, after a few seconds of chlorine addition. This results in the predominant formation of bromoform as a result of bromine incorporation by reaction of HOBr with NOM. Although HOBr is a weaker oxidizing agent than HOCl, it is a more powerful halogenating agent than HOCl. This HOBr reacts with NOM faster than HOCl, and, moreover, the ratio of HOBr to HOCl plays an important role in the speciation of THMs. Hua et al. (2006) [15] reported that the formation of THMs shifts to more brominated species with increasing bromide concentration. As HOBr is a more powerful halogenating agent than HOCl, the brominated THMs are formed first, with bromine consuming the available sites on NOM present in the seawater samples. The speciation trend was similar for the all the temperature studied. The concentration of bromoform increased from 89.62 µg/L to 103.69 µg/L on increasing the temperature from 20^0C to 30^0C and further increased to 119.96 µg/L on increasing the temperature to 40^0C to concentration. Other THMs species also exhibited the monotonous increasing order with temperature and chlorine dose. For 10 mg/L of chlorine dose, BDCM varied from 0.67 µg/L (for 20^0C) to 3.11 µg/L (for 40^0C), whereas, DBCM yield was higher with concentration 11.98 µg/L (for 20^0C) to 33.16 µg/L (for 40^0C).

Bromoform was the only detected THM species observed at the initial stage of the chlorination of the seawater samples, but duration after chlorine addition played a critical role in the speciation of THMs, and both $CHCl_2Br$ and $CHClBr_2$ started to form at a relatively much slower rate as the reaction progressed. Formation of $CHClBr_2$ and $CHCl_2Br$ was found to be favored by higher contact time, chlorine dose, and temperature (**Figure 5a. 5**). $CHClBr_2$ formed relatively more quickly and at a much higher concentration than $CHCl_2Br$. Maximum concentrations of $CHCl_2Br$ and $CHClBr_2$ were found to be 3.15 and 33.16 µg/L, respectively, at 40 ºC with a 10- mg/L Cl_2 dose (**Figure 5a. 6**). Incessant formation of BDCM and DBCM was detected up to several hours after chlorination; by that time, it is supposed that the chlorinated seawater does not have any HOCl molecules available with HOBr for the formation of chloro-substituted THM species. This indicated the possibilities of some indirect reaction pathways for BDCM and DBCM formation. Some mono- and di-chloro-substituted NOM might have formed at the very initial period of chlorination when

HOCl molecules possibly coexisted with HOBr for a very short period, and then the slow reactive mono- and di-chloro-substituted NOM fractions may have undergone bromination to produce the bromo-chloro species of THM at a longer contact time. However, because of the rare availability of adequate HOCl molecules at any time, successive chlorination of NOM and formation of $CHCl_3$ were unfavorable in the chlorinated seawater.

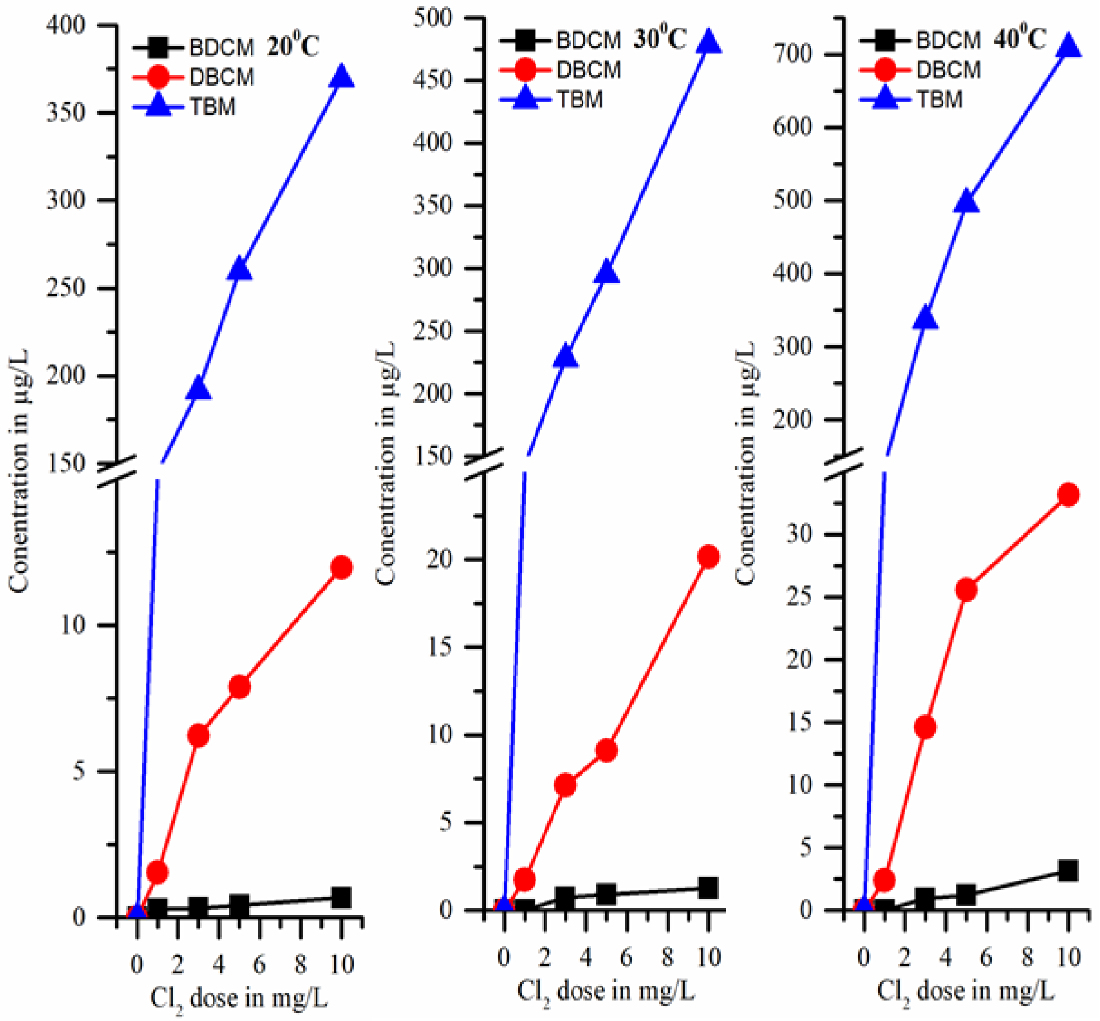


Figure 5a. 4 Comparison of formation of THMs species at different temperatures and chlorine doses.

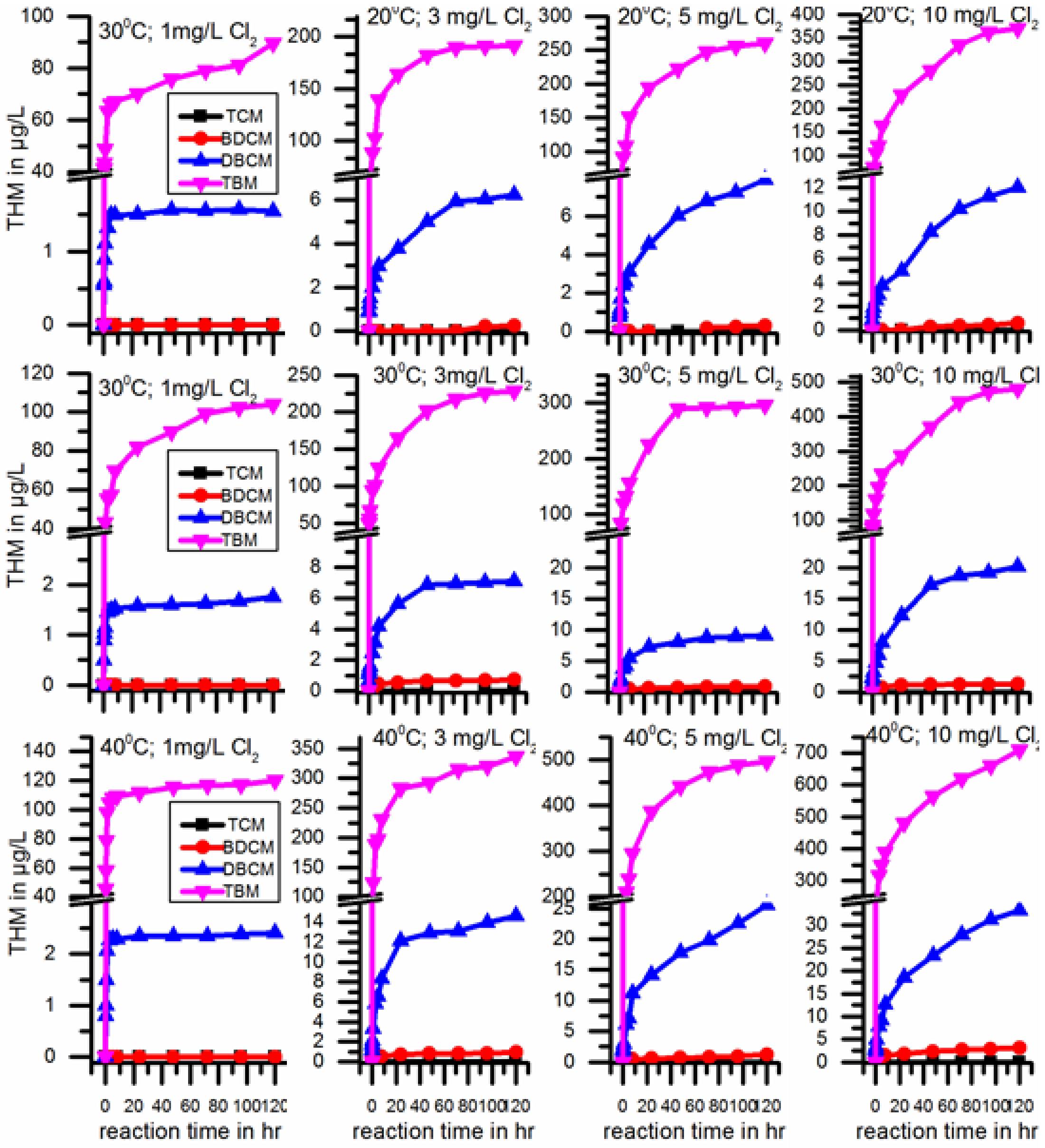


Figure 5a. 5 Kinetics of THM speciation at different chlorination conditions.

5a.2.3 Relationship of chlorine demand with trihalomethane formations

Due to the complexity of seawater, the combined effects of the changes in the complex and heterogeneous water characteristic lead to remarkable temporal and spatial variations in chlorine demand as discussed in the previous chapter. This makes it extremely difficult to predict the chlorine demand of seawater precisely, and thus empirical studies on the chlorine demand must be made at frequent intervals to avoid under/over-chlorination. Though more or less it is possible to quantify the effect of various operational condition viz., Cl_2 dose, contact time, temperature, pH, etc.; it is exceedingly unlike to quantify the chlorine reactivity behavior of numerous unknown complex organic constituents present in the seawater. Moreover, intense qualitative and quantitative site-specific variations in the NOM character and the combined effects of various factors on the NOM reactivity limits the development of any universally acceptable predictive model for chlorine demand and THM formation. NOM variability poses the major limitation in the applicability of various THM prediction models for treated waters [16]. Many studies proposed various complex mathematical models to predict chlorine decay and THM formation in chlorinated cooling and drinking water [17,18]. But universal applicability of these models is not devoid of uncertainties. In some studies [19,20] positive linear correlation of applied chlorine dose and residual chlorine with THM formation has been suggested for THM prediction. Though concentration dependence of chlorine reactivity induces higher Cl_2 demand on increasing chlorine dose, the assumption of linearity in changes of chlorine demand of water with any applied chlorine dose is erroneous. Further, it is hypothetically opposite to propose positive correlation of THM formation with residual chlorine. Chlorine demand caused by the NOM present in the water being the sole responsible factor for the THM formation should be the principal component of any mathematical proposition to predict THM formation in chlorinated water.

Here we have proposed a simplified predictive approach for a possible load of trihalomethane formation at the discharge outlet of an atomic power station exclusively considering the laboratory chlorine demand of the source seawater. Logarithmic correlation of chlorine decay during the chlorination of seawater taken during the study period is presented in **Figure 5a. 6**. It has been observed, irrespective of the period of study, for low-level chlorination of 1 mg/L of Cl_2 dose to the source seawater, the kinetics of chlorine decay showed two distinct phase kinetics. The initial phase fast decay of residual chlorine (**Figure 5a. 6**), can be referred as true organic demand owing to fast reactive fraction of NOM present in the seawater, second sluggish continual chlorine demand attributed to several competitive reactions including reactions of chlorine with low reacting species as well as chlorine self-decomposition leading to secondary “combined chlorine demand”. It is generally accepted that the reaction between chlorine and humic substances, a major component of NOM, is responsible for the production of the organochlorine compound. Humic and fulvic acids show a high reactivity towards chlorine and constitute 50–90% of the total dissolved organic carbon (DOC) in all water systems [21]. The reaction of chlorine with these humic acids may lead to the initial fast reaction rate. Other fractions of the DOC comprise the hydrophilic acids (up to 30%), carbohydrates (10%), simple carboxylic acids (5%) and proteins/amino acids (5%). The reactivity of carbohydrates and carboxylic acids towards chlorine is low, and they are not expected to contribute to the production of organochlorine compounds. Free chlorine reacts with water constituents by three general pathways: oxidation, addition, and substitution [22]. Chlorine can undergo an addition reaction if the organic compound has a double bond. For many compounds with double bonds, this reaction is too slow to be of importance in water treatment. The oxidation reactions with water constituents such as carbohydrates or fatty acids (e.g., oleic acid) are generally slow.

All these slow reacting species results in a slow increase in demand and continual formation of THMs much after chlorine addition. In addition to applied chlorine dose, chlorine demand of raw water mainly depends upon four parameters such as pH, temperature (T), contact time (t) and amount of dissolved organic matter present in water or in other words chlorine demand can be expressed as

Chlorine demand = f (pH, T, DOC, t, Cl_2) (5a.3)

Several investigators have proposed many multi-parameter power function predictive models for THM formation in treated waters which generally takes the following form [17,23].

$THM= k\,[DOC]^a[Br^-]^b[Temp]^c[Cl_2]^d\,(pH)^e\,(Time)^f$ (5a.4)

Which can be written as:

THM = f (DOC, Br, Temp, Cl_2, pH, Time) (5a.5)

In seawater, bromide content is approximately 65 mg/L, which is much excess than the chlorine concentration typically adopted by any thermal plant for seawater chlorination. Moreover, any minor temporal change in seawater bromide concentration, which may occur, is not supposed to shift the equilibrium or alter the kinetics of equation (5a.2). Thus, the contribution of Br^- for THM formation for seawater chlorination can be considered as constant and can be appropriately eliminated from the equation (5a.4). Again, chlorine demand being the function of all other parameters involved, all these can be replaced with it and the equation (5a.5) can be reduced to a single parameter function. In aqueous chlorination, the time course of chlorine decay is always much faster than the comparatively sluggish THM formation. Due to the large difference in their long-term time dependence character, a separate time function (t) must be included to the time dependence THM prediction formula and equation (5a.5) can be rewritten as:

THM = f (Chlorine demand, t) (5a.6)

The above hypothesis forms the basis for the proposed site-specific predictive approach. In the MAPS power plant as described in the previous chapter, the cooling seawater takes only 5-7 min to travel from the point of chlorination to discharge outlet. For such a shorter contact time, separate time factor in equation (5a.6) is also not required, and short-term chlorine demand kinetics of source water alone could be used effectively to predict THM load in the cooling discharge. In the present study, the above hypothesis was tested for its applicability to predict THMs in the cooling discharge water of the MAPS nuclear power plant practicing short duration (5-7 min) low-level chlorination of seawater.

Time course profile of chlorine demand of seawater samples (n=41; all are not shown in **Figure 5a. 6**) collected during the entire study period fits well to logarithmical correlation with R^2 values ranges 0.8775-0.9945. The logarithmic correlation of chlorine demand can be generalized as,

Chlorine Demand = A + B * ln t (5a.7)

Where,

A: Chlorine demand at time t= 0, can be taken as the instantaneous chlorine demand responsible for the initial phase kinetics, referred to as True organic demand constant.

B: Combined chlorine demand constant, is the time-dependent factor resulting from the chlorine consumption through various pathways including self- decompositions.

$B = B_o + B_n$, where, (5a.8)

B_o: Chlorine demand factor for slow reactive organic fraction, B_n: Non-organic Chlorine demand.

For low-level Seawater chlorination of 1 mg/L, the values observed for 'A' varied from 0.09-0.41, but there was a small temporal variation in the constant 'B' associated with "combined chlorine demand" with $\Delta B_{max} = 0.06$. Therefore, contribution of the time variable decay factor 'B* ln t' toward change in THM formation for short contact time could be replaced with another constant. Further, since for shorter contact time, 'A' representing the fast-reactive organic fraction of DOC was the major contributor of THM formation and B comprising organic demand corresponding to slow relative fraction was mostly due to non-organic chlorine demand, i.e. $B_n >> B_o$. Thus, for a short time period with low-level chlorination of seawater, the formation of THM could be treated as a function of only 'A' and mathematically generalized to

$[TTHM] \alpha A \rightarrow [TTHM] = k * A$ (5a.9)

Value of 'A' for the respective chlorinated water could be determined from the logarithmic correlation equations of chlorine decay as in **Figure 5a. 6.**

Substituting the value of 'k' obtained from linear regression of the values of 'A' for a number of experimental samples and real sample collected during the different period of study with observed trihalomethane concentrations, the above equation becomes,

$[TTHM] = 104.45 \pm 9.6 * A$ (5a.10)

The proposed hypothesis can be used to obtain 'k' values for the source water to establish its applicability to similar chlorination practice. The calculated THM concentration using the above equation and observed mean THM concentration in the laboratory chlorination experiments are presented in **Figure 5a.7** which showed a good linear correlation. Although load of THM formation known to be dependent on various physicochemical characteristics of water and operational variables, chlorine demand itself as a function of all independent variables which exclusively responsible for THM formation can alone be fairly used to predict the of THM formation potential of the seawater.

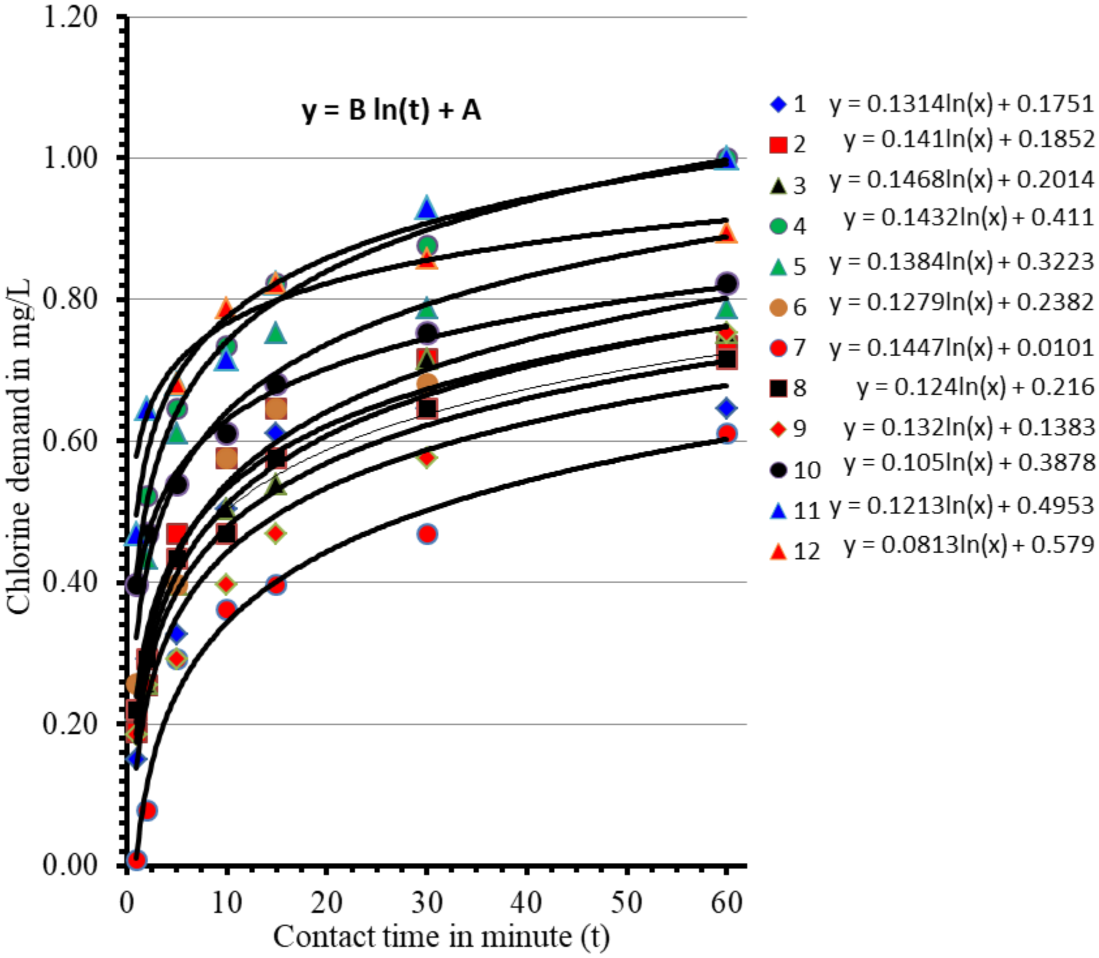


Figure 5a. 6 Logarithmic fitting of chlorine decay profile (R2 = 0.8775-0.9945) during chlorination of seawater samples collected during the different time of study period

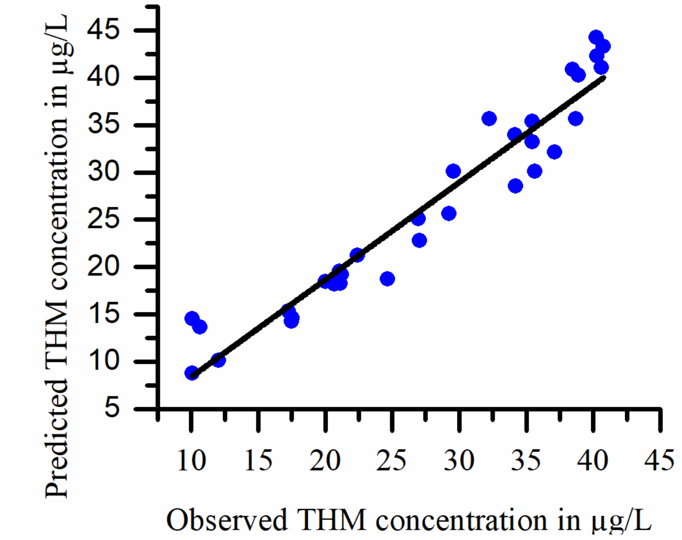


Figure 5a. 7 Linear correlation of observed and predicted TTHM concentrations using the proposed simplified equation which considers only chlorine demand (R2 = 0.9635)

5a.4 Conclusion

Chlorine demand of the source seawater needs to be monitored at frequent intervals to avoid under/over-chlorination. Bromoform constitutes 96-98% of the TTHM formed in the chlorinated Seawater. Data on short time course chlorine demand of intake seawater alone can be effectively used to predict the THM concentration with acceptable uncertainties. The results of the present study have shown that on chlorination, seawater has the potential to form significant levels of THMs within a very short contact time and can linearly increase with temperature, applied Cl_2 doses, and contact time. Although the concentration of THMs formed increased with increasing Cl_2 dose, it was observed that the percentage of chlorine-equivalent halogen incorporation into NOMs decreased possibly because of the limiting amount of fast reactive NOM fractions. Higher temperatures not only increased the rate of THM formation but also enhanced the overall yield. The effect of temperature on the total yield of THMs is found to be more significant for temperature change at higher ranges. Formation of chloroform, if any, remained below the detectable limit; very low concentrations of DBCM and BDCM were formed and favored by higher temperatures, increased Cl_2 doses, and increased reaction time. Formation of bromoform dominated at all investigated conditions. The TTHM formation rate followed a very high initial rate and considerably subsided, 5 h after chlorination. The overall formation of different THM species followed the order: $CHCl_2Br < CHClBr_2 < CHBr_3$.

Chapter 5b

Impact of open storage on chlorination and THMs formation

Abstract: Changes in water quality upon open storage of groundwater and its impact on chlorination and chlorination by-products (CBPs) formation was investigated. Water quality descriptors such as temperature, pH, Chlorophyll-a and dissolved oxygen contents of groundwater underwent substantial alteration when stored in a reservoir. Dissolved organic content (DOC) measured in the two water sources studied namely subsoil water of Palar river (RVR), and water samples from an open reservoir (RSR) varied from 0.41 to 0.95 mg/L and 0.93 to 2.53 mg/L respectively. Although, DOC demonstrated wide variations, UVA_{254} values of RVR (0.022-0.067 cm^{-1}) and RSR (0.037-0.077 cm^{-1}) did not display reciprocal variations. Chlorine demand (CD) of RSR was always higher than that of RVR for the corresponding sampling period. Average trihalomethanes formation for RSR was 50-80% higher compared to RVR and thus poses an enhanced health risk. An appreciable amount of bromide present in these water sources (0.15 – 0.26 mg/L in RVR and 0.17 -0.65 mg/L in RSR) have resulted in the non-selective distribution of four THM species. The formation of more toxic brominated THM due to chlorination of these near coast drinking water sources must be taken as a decisive factor for the choice of water disinfection regime.

5b.1 Introduction

Reservoirs are manmade lakes, primarily used for storing water for different purposes such as uninterrupted drinking water supply, industrial water requirements, hydroelectric power generation, and irrigation. Flowing water when stilled in reservoirs undergoes physical, chemical & biological changes requires a different water treatment regime from that of original source water particularly when the water is to be used for drinking. For example, the temperature of stream water which is generally dynamic, varies only a couple of degree around the year, whereas it varies widely in a reservoir depending on the climatic condition of the area [24]. Same is true for nutrients, chlorophyll-a (Chl-a), dissolved oxygen (DO) and other associated chemical and biological parameters [24]. Due to the stagnant nature of the water in the reservoir, we can assume that a certain amount of contamination or deterioration in the water quality will occur as compared to the subsoil river water. Of course, the extent of deterioration in water quality depends upon residence time of the water decided by the storage capacity, amount and sources of the water flowing into it.

Chlorination is a widely used drinking water treatment process to inactivate many waterborne pathogens and to combat biofouling in industrial cooling water systems. However, in addition to its intended function, chlorine reacts with organic compounds in the water to produce halogenated by-products including trihalomethanes (THMs), haloaceticacids (HAAs), haloacetonitriles (HANs), haloketones (HKs) [25]. Among these, THMs are the most commonly found chlorination byproducts (CBPs). Exposure to these disinfection byproducts (DBPs) has been associated with adverse effects on human health including bladder cancer [26,27]. After the emergence of pressing issues like carcinogenic cell reproduction, genetic mutation, and tissue damage, the U.S. Environmental Protection Agency (EPA) instituted the stage-I disinfection by-product regulation (DBPR) during the late 1990s, and stage-II DBPR was issued in 2006 limiting the total THMs to $\leq$ 80 μg/L. The types & and yield of DBPs such as THMs varies with the type of disinfectant used and the nature of the source water [28]. The DBPs concentration and speciation are also affected by many water quality determinants (Type and quantity of dissolved organic matter (DOM), pH, bromide, ammonia, Nitrite concentration, and water temperature) and operational parameters (disinfectant dose and type, reaction time, etc.). Generally, THMs formation increases with an increase in chlorine dose and DOM concentration [25,29]. In India, traditional open reservoirs for water fed by rainwater or river water are important sources for drinking water supply both in rural and urban areas. In open reservoirs storage facilities, water degradation has been a recognized concern for many decades [30]. Since the volume of water in storage facility normally is large compared to the amount of exposed surface area, the effect of the wall and floor on disinfectant decay are normally not significant. Thus, disinfectant decay and byproduct formation in storage facilities normally can be attributed to bulk decay which mainly depends on the source water physicochemical characteristic rather than to wall effects. Covering an open reservoir or replacing it with a covered storage facility can reduce or eliminate the potential for direct entry of contaminants and deterioration in the water quality. However, most reservoirs remain uncovered due to the capital cost involved in covering them and the difficulty in clearly quantifying the public health benefits accrued from covering. Direct input by runoff or internal growth of algae increases the organic material load in the open storage facilities. Additionally, microorganisms can enter from outside sources such as poorly constructed or inadequately maintained storage facility & also can be introduced into open reservoirs from wind-blown dust and debris. In addition, groundwater having good nutrient content when stagnated and exposed to sunlight in an open reservoir becomes eutrophic leading to a proliferation of algae due to photosynthesis. Extracellular matter from the decay of these algae increases the organic load of the water, which serves as THM precursors [31]. Organic matter, such as leaves and pollen also append to it and are a concern in open reservoirs. It should be noted, however, that DBP levels do not necessarily increase in all open reservoirs. High trihalomethanes formation potential (THMFP) values were not correlated with peak algal levels in studies conducted in Seattle at LADWP's Silver Lake reservoir [30], which indicated that algae were not reactive causative agents contributing to DBP formation. Other types of organic substrate also have the potential to affect DBP formation. Some utilities have observed no significant changes, and some have experienced decreases in DBP levels across their open reservoirs [32]. One utility has conjectured that DBP levels may decrease through volatilization or oxidation of precursors by heterotrophic bacteria [32]. Study on the inter-river comparison on the per unit algal contribution towards yield of THM by Jack et al. (2002) [33] revealed that potential of carbon fluxes arising from the algal senescence was much higher than the carbon required to account for TTHM formation. Much of the algal carbon is labile and therefore likely to be respired. Due to different source water quality and diverse water treatment processes within different waterworks, the key parameters controlling DBPs formation may vary from place to place. Identification of impact of storage facilities on water qualities and strategies to minimize adverse effect are required to ensure that the water quality meets the regulatory guidelines and does not degrade in the distribution system. As there are many potential variables involved, investigation on the implication of storage facilities on water quality and strategies to minimize adverse effects are required to ensure that it meets the regulatory guidelines to deliver safe water. The present study was focused on the total trihalomethanes formation potential (TTHMFP) of two different water types, mainly, upon open storage of subsoil water (1) how primary water quality determinant such as pH, temp, chlorophyll-a, dissolved organic carbon (DOC) undergo changes (2) How these parameters influences TTHMFP of both the water types (3) whether DOC and UV_{254} can be correlated with chlorine demand and THMs formation and (4) finally, the role of bromide in the distribution of THMs species.

5b.2 Results and Discussion

The main factors that influence the formation of DBPs include contact time, chlorine demand (CD), temperature, pH, the concentration of precursors and bromide ions. There were considerable differences in these parameters between RVR and RSR. In general, both RSR and RVR had moderate DOC with an average of 1.68 & 0.82 mg/L and UVA_{254} with an average of 0.057 and 0.049 cm^{-1} respectively. The wide variations in DOC values of both the water types were not quantitatively reciprocated in the respective UVA_{254} variations. Among the three main categories of problems i.e chemical, microbiological, and physical that occur in the storage facilities, loss of disinfectant residual or chlorine demand and formation of disinfection by-products are the most common chemical problems. For the same source water, CD is a function of both time and initial chlorine dose. Chlorine demand values for both the source water types at different initial chlorine concentration and time intervals during the two years

(2012-2013) of study are presented in **Figure 5b. 1**. It was observed that chlorine decay was slower and hence demands were lower in the case of RVR as compared to RSR with value ranged from 1.11 to 2.63 mg/L and 1.46 to 4.36 mg/L respectively for RVR and RSR samples for a Cl_2 dose of 5 mg/L and contact time of 6 h. It was obvious from the comparative higher chlorophyll-a content in the open reservoir water (**Table 5b. 1**) that, high biological activities as expected in the reservoir have led to the increase in organic content in the water and thus caused higher chlorine demand than that of RVR. Therefore, a higher amount of chlorine will be required for RSR to achieve the same desired residual as compared to RVR. However, the extent of compensation for the organic content in both the water types was different owing to the differences in their chlorine reactivity. Temporal variations in TTHMF under different chlorination conditions (**Figure 5b. 2**) showed that THM formation was always higher for RSR than that of RVR for all chlorination conditions. Though higher THM formation was always observed for RSR, the magnitude of THM formation was not quantitatively reciprocated with the increase in chlorine demand, indicating the presence of non THM forming precursor constituents in the algal organic content in RSR. Multi-parameter dependence of THM formation might result in net facilitating effect or opposing effect when simultaneous temporal changes occur in these parameters. This factor attribute to the random temporal behavior of TTHMF of both the water types and no seasonal trend could be established. On increasing residence time from 6 h to 24 h, both RSR and RVR exhibited an increase in TTHMF irrespective of the initial chlorine concentration of 3 or 5 mg/L. However, monthly time course increment profile was arbitrary, for example, RSR displayed only an increase of ~10% (11.58 µg/L) in the month of June-2012 whereas nearly 62%

increase was observed in July-2012 for 3 mg/L Cl_2 dose. Similar results were observed for higher chlorine dose and Palar subsoil water also. As expected, temperature and pH values for reservoir water were always observed to be distinctly higher than the RVR (**Table 5b. 1**).

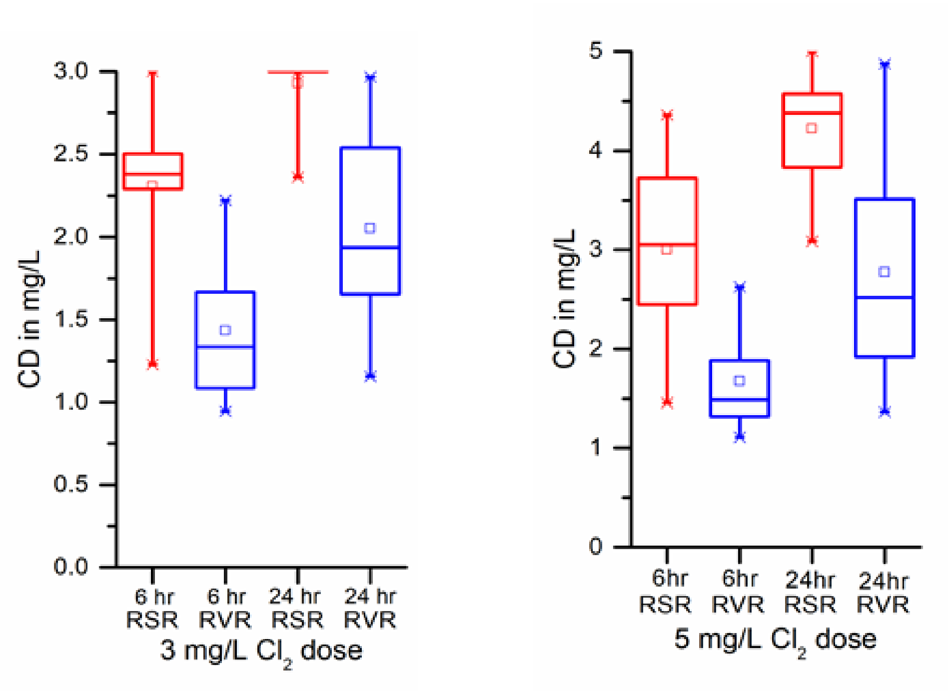


Figure 5b. 1 Comparison of chlorine demand values for RSR and RVR at different chlorination dose and contact time

Higher pH observed in the reservoir water as compared to the Palar water is apparently due the photosynthetic activity by phytoplankton and macrophytes as per the following reactions [34]. Continuous uptake of carbon dioxide generated due to the dissociation of HCO_3^- by the phytoplankton and macrophytes drives the net reaction (eq. 5b.1) towards right and CO_3^{-2} hydrolyzes in water to produce hydroxyl ion (eq. 5b.2) which gradually assimilates in the reservoir water to increase the pH.

$$2HCO_3^- \leftrightarrow CO_2 + CO_3^{-2} + H_2O \qquad (5b.1)$$

$$CO_3^{-2} + H_2O \leftrightarrow HCO_3^- + OH^- \qquad (5b.2)$$

Table 5b. 1 Summary of water quality parameters (min-max) of RVR and RSR collected during the spread of the study period (n=21)

Water Quality Parameters	RVR	RSR
Temp (^{0}C)	27.0-32.8	27.5-34.7
pH	7.1-7.6	8.1-9.0
Chl-a (mg/m^3)	0.91-1.93	2.84-20.55
Br- (mg/L)	0.09-0.26	0.15-0.65
DOC (mg/L)	0.41-0.95	0.93-2.56
UVA$_{254}$ (cm^{-1})	0.022-0.067	0.037-0.077
SUVA$_{254}$ (L mg $^{-1}$ m^{-1})	5.37-7.05	3.08-3.98
CD$_{6\text{ h/3 mg/L}}$ (mg/L)	0.94-2.22	1.23- >3.00
CD$_{6\text{ h/5 mg/L}}$ (mg/L)	1.11-2.62	1.46-4.36
TTHMF$_{6\text{ h/3 mg/l}}$ (µg/L)	26.3-120.3	44.2-190.2
TTHMF$_{24\text{ h/3 mg/L}}$ (µg/L)	54.7-246.5	68.9-265.2
TTHMF$_{6\text{ h/5 mg/L}}$ (µg/L)	36.3-153.4	40.1-210.4
TTHMF$_{24\text{ h/5 mg/l}}$ (µg/L)	62.9-335.3	91.82-370.4

Leaching of hydroxides and carbonates from concrete surfaces of the storage facilities also cause the pH level to increase to some extent. pH affects the ionization equilibrium of oxidants which alter the species composition, i.e. among OCl^-, OBr^-, HOCl, and HOBr. These oxidant species have a varying degree of reactivity and can induce structural modification of organic precursor thereby changing their propensity for THM production. In general, the rate of THM production increases with pH [35]. A threefold increase in the reaction rate per unit increase in pH was reported by [36]. Formation of THM mainly depends on the last step base catalysis reaction favored at higher pH as in the haloform reaction. Decrease in THM formation as a result of lowering pH has been noted by many researchers [37,38]. At lower pH, organic matters get condensed, and at higher pH it undergoes structural expansion exposing the chromophoric sites for the reaction [39]. This change in configuration might also result more NOM sites to come in contact with chlorine favoring the THM formation. The algal biochemical composition also plays an important role in determining the TTHM yield [40]. This is supported by the previous study showing higher TTHMFP for diatoms than green algae under same chlorination conditions [41]. Aquatic humic acids contain more aromatic carbon than algal derived carbon thus has higher TTHMFP [42,43]. These are possible factors for which higher CD of RSR was not proportionally reflected on the magnitude of trihalomethanes formation in RSR for corresponding chlorination conditions. However, compared to RSR and RVR, CD and TTHMFP of RSR were always observed to be higher.

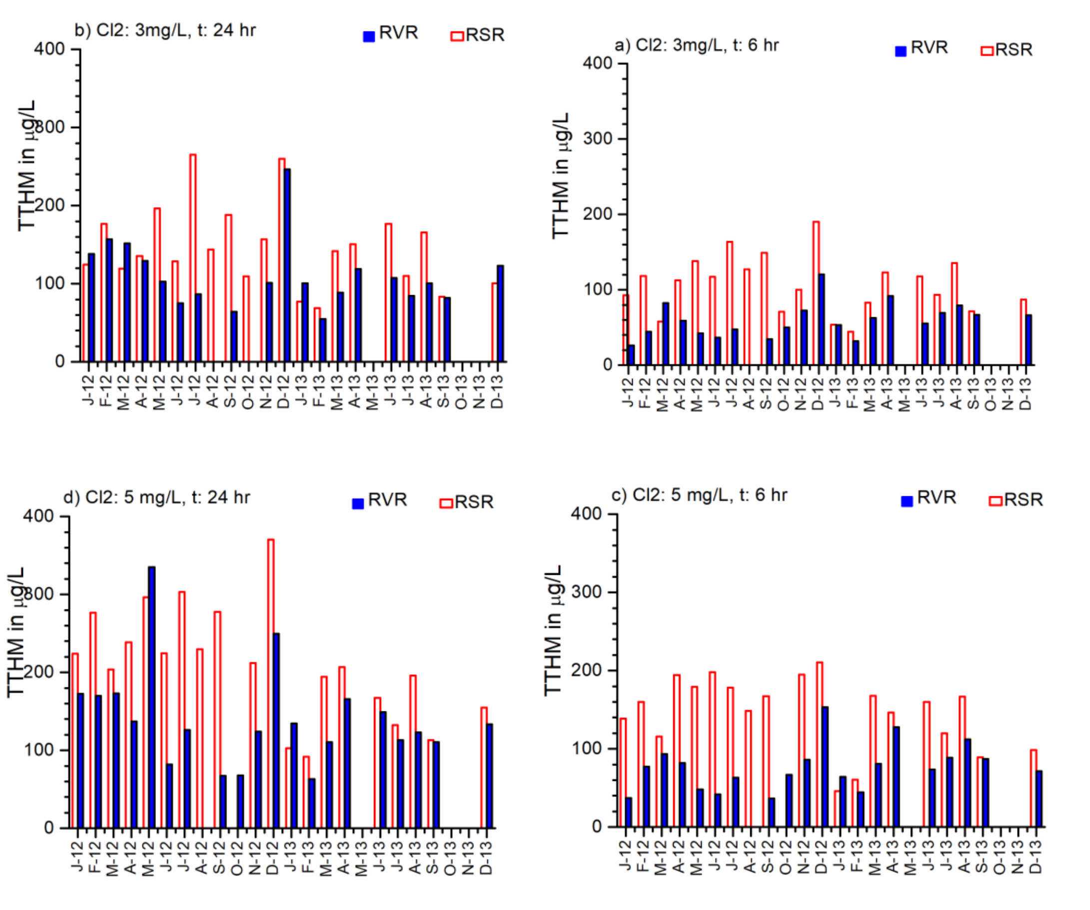


Figure 5b. 2 Temporal variations and comparison of TTHM formation potential of RVR and RSR at different chlorination conditions.

Temporal variations in UVA_{254} values are presented in **Figure 5b.3.** The results showed that its magnitude and the temporal trend was similar for both RSR & RVR. As discussed previously, these two water sources exhibited low UVA_{254} absorption. In water with high UVA_{254} such as those containing humic fractions, it is often observed that UV absorbance at 254 is strongly correlated to DOC content and trihalomethanes formation [44]. Such a trend was not found in our study possibly because most of the NOM in these waters are non-UV absorbing fractions. Water samples having DOC concentration ranging from 0.1 to 0.8 mg/L generally exhibited a low and narrow range of UVA (<0.010 cm^{-1}) indicating UVA_{254} is almost independent of DOC [45]. **Figure 5b. 4** and **Figure 5b. 5** demonstrated the comparative account of UVA_{254} with respect to TTHMFP and chlorine demand (5 mg/L of Cl_2, 24 h) for both the water types. UV_{254} absorbing groups usually contain free electrons in the oxygen and sulfur atoms, conjugated C=C bonds and aromatic carbon [46]. Because of the ease of measurement, UVA_{254} served as a proxy for aromatic content in the dissolved organic matter and correlated with trihalomethanes formation as reported by Fram et al. (1990) [47]. NOM has distinct characteristics associated with its origin viz. vegetation, soil, wastewater, etc. For example, dissolved organic carbon from aquatic algae has relatively large nitrogen content, low aromatic carbon, and low phenolic contents. On the other hand, terrestrially derived DOC is relatively low in nitrogen content but rich in the aromatic and phenolic component. Thus, the aromatic content which is believed to be the major reactive content varies with the source of generation [48]. When freshwater is impounded in reservoirs, the longer hydrologic residence time (typically in the order of months to year compared to a few hours to a week in riverine systems) may be long enough to allow transformation of allochthonous carbon input [49]. Additionally, NOM is formed by autochthonous production from algal and microbial activity. Autochthonous organic materials derived from algal or microbiological productivity tend to be more aliphatic with much higher nutrient inclusion. Phytoplanktons, in particular, are the major producers of autochthonous DOC in reservoirs [50]. The relative influence each end-member class determines the bulk chemical properties of the DOC, including hydrophobicity and hence oxidant reactivity [51,52]. Many studies which correlated UV_{254} and $SUVA_{254}$ with TTHM of the water have suggested that with low to the moderate value of UV_{254}, the usefulness of these surrogate parameters for prediction of TTHM formation is limited [53,54]. In our study, we did not observe any correlation of UVA_{254} with TTHMFP and chlorine demand of both the source water (**Figure 5b. 4 & 5b. 5**). Water having SUVA values < 1.5-2.0 L mg^{-1} m^{-1} generally contains hydrophilic, non-humic and smaller molecular weight NOM moieties [55]. SUVA values for RSR and RVR were higher than this value which ranged between 3.09-3.98 L mg^{-1} m^{-1} and 5.37-7.05 L mg^{-1} m^{-1} respectively. Thus, it appears that some special NOM moieties, most probably of non-humic, non-UV absorbing and hydrophilic nature are responsible for the THM formation in these source water. In addition, these moieties possibly comprised only a small portion of all NOM and therefore DOC also showed no correlation with THMs.

Among the number of determinants that affect the DBPs formation and speciation, bromide level in raw water influences the species distribution to relatively greater extent [56]. The effects of bromide present on the trihalomethanes formation potential for both the waters were also investigated. The typical range of bromide in fresh water varies from trace amounts to about 0.5 mg/L [57]. Bromide content of the

Palar subsoil water ranged between 0.15 – 0.26 mg/L and relatively higher values were observed for reservoir water (0.17 -0.65 mg/L).

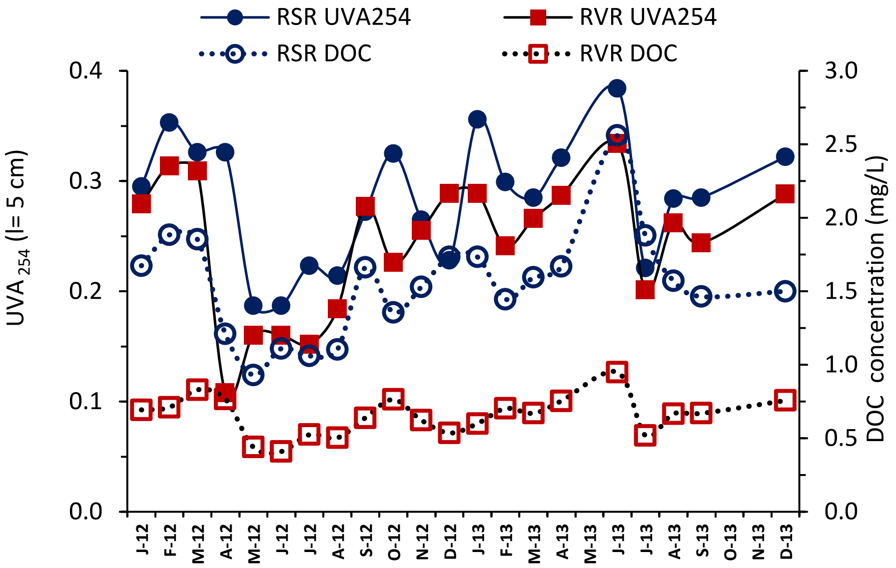


Figure 5b. 3 Temporal variations and comparison of UVA$_{254}$ with DOC of both water type

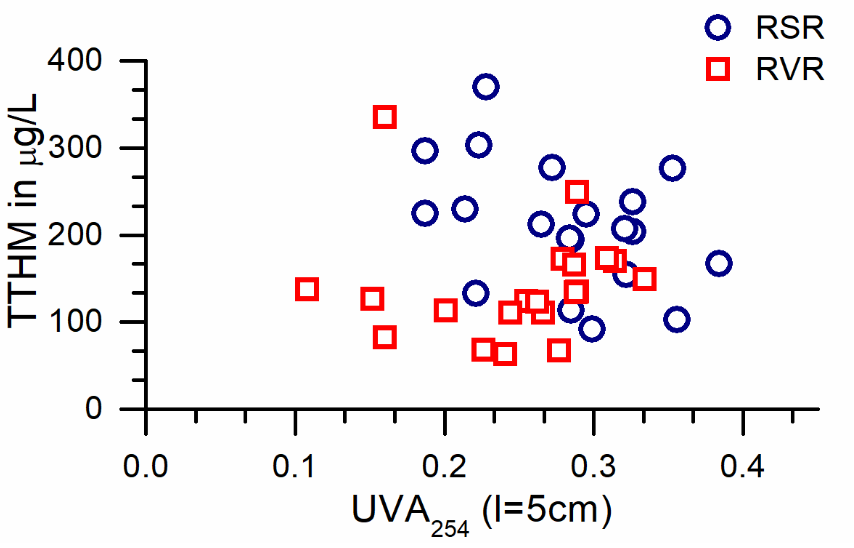


Figure 5b. 4 Correlation of UVA$_{254}$ with TTHM formation at 5 mg/L of Cl_2 dose and contact time of 24 h

At different chlorine dose and reaction time, speciation of THMs for both the water types are depicted in **Figure 5b. 6 (a)** and **5b. 6 (b)**. Generally, chloroform is the major contributor of THMs with a relatively lower amount of other species in freshwater chlorination, in contrast, bromoform constitutes more than 95% of THMs in the chlorinated seawater [19] owing to its higher bromide content (~ 65 mg/L). However, being located near the coast, an appreciable amount of bromide is present in these water sources, which might be derived from the seawater aerosol. The coexistence of HOCl and HOBr formed due to oxidation of Br^- by HOCl during chlorination has resulted in THM species to be non-selectively distributed among all the four species and no preferential formation of any particular species was observed. The abundant formation of partial brominated THM in these source water associated with higher level of toxicity can be a concern for adopting chlorination as a pathogen control measure. Previous studies have reported that the presence of bromide shifts the species distribution towards Br-containing THMs as well as it also increases total THM yield [15,58]. Furthermore, the bromine-containing DBPs are known to be more toxic than their chlorine counterpart. Bromide present in the water gets oxidized by HOCl forming hypobromous acid (HOBr) which is a better halogenating species at natural water pH. The instantaneous oxidation of bromide to HOBr and easier formation of Br-C bond than Cl-C bond results in enhanced overall TTHM yield and greatly alters the species composition of THMs as was observed in the present case [59]. No distinct difference in the species distribution character was observed between RSR and RVR. At chlorine dose of 3 mg/L, the species pattern almost remained constant irrespective of reaction time and water type whether RSR or RVR. However, at a higher chlorine dose of 5 mg/L, distribution of species shifted more towards the brominated analog in RSR as compared to RVR. Another important observation with respect to THM formation mechanism was that on increasing chlorine dose and contact time, the contribution of bromodichloromethane (BDCM) toward overall TTHM increased irrespective of water type, which demands further investigation.

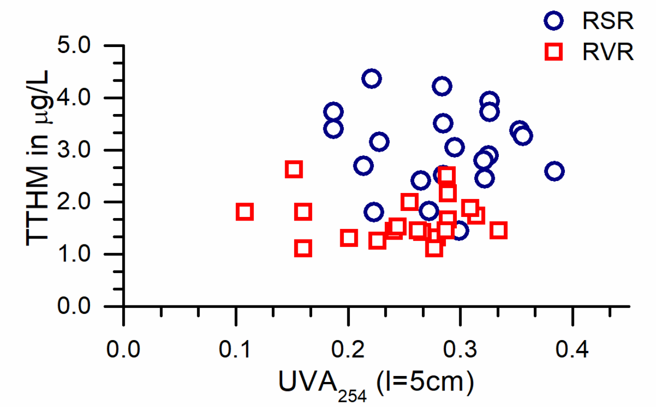


Figure 5b. 5 Correlation of UVA254 with chlorine demand for 5 mg/L of Cl2 and contact time of 6 h.

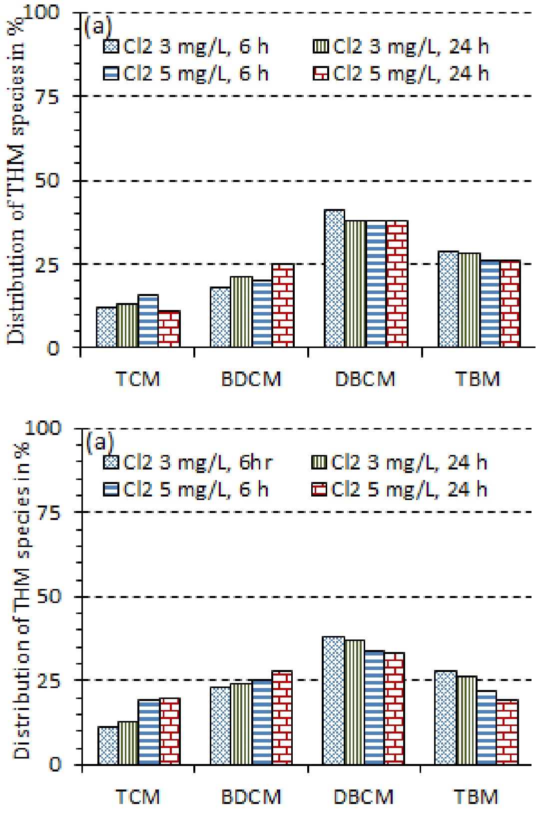


Figure 5b. 6 Percentage distribution of THM specis in chlorinated water; (a): RSR for (i) Cl2 3 mg/L, 6 h (ii) Cl2 3 mg/L, 24 h (iii) Cl2 5 mg/L, 6 h (iv) Cl2 5 mg/L, 24 h, and (b): RVR for for (i) Cl2 3 mg/L, 6 h (ii) Cl2 3 mg/L, 24 h (iii) Cl2 5 mg/L, 6 h (iv) Cl2 5 mg/L, 24 h.

5b.3 Conclusion

Disinfection by-products were higher in RSR as compared to RVR, which suggested that chlorination of open storage water might lead to a higher health risk. Presence of THM forming precursor constituents in the algal-derived organic content of RSR was insignificant. Thus, the increase in THM formation was not quantitatively reciprocated with the extent of the difference in chlorine demand of both RSR and RVR, suggesting the presence of organic matter with different chemical compositions. Temperature & pH values of open reservoir water were observed to be higher than the original river water source and were generally associated with high CD and THM formation. DOC content and UVA_{254} did not correlate well with trihalomethanes formation for both the water types and thus could not be taken as a surrogate parameter for prediction of trihalomethanes formation potential of the studied water. The distribution pattern of THMs species was not selective to chloroform unlike that generally observed for freshwater chlorination. Presence of appreciable amount of bromide in these water sources (0.15 – 0.26 mg/L in RVR and 0.17 -0.65 mg/L in RSR) have resulted in non- selective distribution of the four THM species. The extent of bromide present in the raw water must be taken into consideration if chlorine has to be used for disinfection and more so if the water source is in close proximity to coastal areas. The abundant formation of partial brominated THM which are generally associated with a higher level of toxicity has to be considered carefully during the chlorine disinfection of water from both sources.

References

[1] S. Fam, M.K. Stenstrom, Precursors of Non-Volatile Chlorination By-Products, J. (Water Pollut. Control Fed. 59 (1987) 969–978.

[2] S.K. Gang, D. C., Clevenger, T. E., & Banerji, D.C. Gang, T.E. Clevenger, S.K. Banerji, Modeling Chlorine Decay in Surface Water, J. Environ. Informatics. 1 (2003) 21–27.

[3] D.A. Hansell, C.A. Carlson, R.M.W. Amon, Biogeochemistry of marine dissolved organic matter, Elsevier, 2002.

[4] M. Fabbricino, G. V. Korshin, Formation of disinfection by-products and applicability of differential absorbance spectroscopy to monitor halogenation in chlorinated coastal and deep ocean seawater, Desalination. 176 (2005) 57–69.

[5] H.A. Jenner, C.J.L. Taylor, M. Van Donk, M. Khalanski, Chlorination by-products in chlorinated cooling water of some European coastal power stations, Mar. Environ. Res. 43 (1997) 279–293.

[6] Michael J. Plewa, E.D. Wagner, S.D.R. And, J. Alfred D. Thruston, Y.-T. Woo, A.B. McKague, Chemical and Biological Characterization of Newly Discovered Iodoacid Drinking Water Disinfection Byproducts, (2004).

[7] D.H. Choi, J.S. Park, C.Y. Hwang, S.H. Huh, B.C. Cho, Effects of thermal effluents from a power station on bacteria and heterotrophic nanoflagellates in coastal waters, Mar. Ecol. Prog. Ser. 229 (2002) 1–10.

[8] T. Hoepner, S. Lattemann, T. Höpner, S. Lattemann, Chemical impacts from seawater desalination plants — a case study of the northern Red Sea, Desalination. 152 (2003) 133–140.

[9] A.G.I. Dalvi, R. Al-Rasheed, M.A. Javeed, Haloacetic acids (HAAs) formation in desalination processes from disinfectants, Desalination. 129 (2000) 261–271.

[10] D.T. Williams, G.L. LeBel, F.M. Benoit, Disinfection by-products in Canadian drinking water, Chemosphere. 34 (1997) 299–316.

[11] A.D. Nikolaou, S.K. Golfinopoulos, M.N. Kostopoulou, T.D. Lekkas, Decomposition of dihaloacetonitriles in water solutions and fortified drinking water samples, Chemosphere. 41 (2000) 1149–1154.

[12] N.M. Ram, Y.G. Mussalli, C. Winston, Total Trihalomethane Formation during Targeted and Conventional Chlorination of Seawater for Biofouling Control, Res. J. Water Pollut. Control Fed. 62 (1990) 789–795.

[13] G.T.F.T.F. Wong, J.A.A. Davidson, The fate of chlorine in sea-water, Water Res. 11 (1977) 971–978.

[14] C.J.L.L. Taylor, The effects of biological fouling control at coastal and estuarine power stations, Mar. Pollut. Bull. 53 (2006) 30–48.

[15] G. Hua, D.A. Reckhow, J. Kim, Effect of Bromide and Iodide Ions on the Formation and Speciation of Disinfection Byproducts during Chlorination, Environ. Sci. Technol. Technol. 40 (2006) 3050–3056.

[16] D.A. Reckhow, P.C. Singer, Mechanisms of organic halide formation during fulvic acid chlorination and implications with respect to preozonation, in: R.L. Jolley, H. Gorcher, D.H. Hamilton (Eds.), Water Chlorination Environ. Impact Heal. Eff., Ann Arbor Science, 1985: pp. 1229–1257.

[17] E.E. Chang, P.C. Chiang, S.H. Chao, Y.L. Lin, Relationship between chlorine consumption and chlorination by-products formation for model compounds, Chemosphere. 64 (2006) 1196–1203.

[18] R. Rajamohan, E. Vinnitha, V.P. Venugopalan, S. V. Narasimhan, Chlorination by-products and their discharge from the cooling water system of a coastal electric plant, Curr. Sci. 93 (2007) 1608–1612.

[19] A. Abdel-Wahab, Formation of Trihalomethanes during Seawater Chlorination, J. Environ. Prot. (Irvine,. Calif). 01 (2010) 456–465.

[20] E.M. Thruman, Organic Geochemistry of Natural Waters., 1st ed., Academic Publisher, 1985.

[21] J.D. Johnson, J.N. Jensen, THM and TOX Formation: Routes, Rates, and Precursors, J. Am. Water Works Assoc. 78 (1986) 156–162.

[22] USEPA, National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfection Byproducts Rule; Final rule, (2006) 399–493.

[23] J. Sohn, G. Amy, J. Cho, Y. Lee, Y. Yoon, Disinfectant decay and disinfection by-products formation model development: chlorination and ozonation by-products, Water Res. 38 (2004) 2461–2478.

[24] K.K. Satpathy, Studies on the chemical features of cooling water systems in the context of scaling, biofouling and corrosion control, Madras University, India, 1996.

[25] J. Hu, H. Song, J.W. Addison, T. Karanfil, Halonitromethane formation potentials in drinking waters, Water Res. 44 (2010) 105–114.

[26] M.J. Rodriguez, J.B. S??rodes, P. Levallois, Behavior of trihalomethanes and haloacetic acids in a drinking water distribution system, Water Res. 38 (2004) 4367–4382.

[27] E.R. Blatchley, D. Margetas, R. Duggirala, Copper catalysis in chloroform formation during water chlorination, Water Res. 37 (2003) 4385–4394.

[28] H. Whitaker, N. Best, M.J. Nieuwenhuijsen, J. Wakefield, J. Fawell, P. Elliott, Modelling exposure to disinfection by-products in drinking water for an epidemiological study of adverse birth outcomes, J. Expo. Anal. Environ. Epidemiol. 15 (2005) 138–146.

[29] E.F. Xie, Disinfection byproducts in drinking water: formation, Analysis and control, Lewis Publisher, Washington DC, 2004.

[30] USEPA, Uncovered finished water reservoir guidance manual:United States Environmental Protection Agency guidance manual-815-R-99-01, 1999.

[31] R.C. Hoehn, D.B. Barnes, B.C. Thompson, C.W. Randall, T.J. Grizzard, P.T.B. Shaffer, Algae as Sources of Trihalomethane Precursors, J. Am. Water Works Assoc. 72 (1980) 344–350.

[32] AWWA, Deterioration of water quality in large distribution reservoir (Open reservoirs) committee report, J. Am. Water Work Assoc. 75 (1983) 3313–18.

[33] J. Jack, T. Sellers, P.A. Bukaveckas, Algal production and trihalomethane formation potential: an experimental assessment and inter-river comparison, Can. J. Fish. Aquat. Sci. 59 (2002) 1482–1491.

[34] C.E. Boyd, V.K. Pillai, Water quality and fish production., in: Water Qual. Manag. Aquac., CMFRI special Publication, 1985: pp. 1–44.

[35] M.P. Abdullah, C.H. Yew, M.S. Bin Ramli, Formation, modeling and validation of trihalomethanes (THM) in Malaysian drinking water: A case study in the districts of Tampin, Negeri Sembilan and Sabak Bernam, Selangor, Malaysia, Water Res. 37 (2003) 4637–4644.

[36] M.C. Kavanaugh, A.R. Trussell, J. Cromer, R.R. Trussell, An Empirical Kinetic Model of Trihalomethane Formation: Applications to Meet the Proposed THM Standard, J. Am. Water Works Assoc. 72 (1980) 578–582.

[37] C.J. Peters, R.J. Young, R. Perry, Factors influencing the formation of haloforms in the chlorination of humic materials, Environ. Sci. Technol. 14 (1980) 1391–1395.

[38] R.J. Garcia-Villanova, C. Garcia, J.A. Gomez, M.P. Garcia, R. Ardanuy, J. Alfonso Gomez, M. Paz Garcia, R. Ardanuy, Formation, evolution and modeling of trihalomethanes in the drinking water of a town: I. At the municipal treatment utilities, Water Res. 31 (1997) 1299–1308.

[39] M.L. Pace, I. Reche, J.J. Cole, A. Fernández-Barbero, I.P. Mazuecos, Y.T. Prairie, pH change induces shifts in the size and light absorption of dissolved organic matter, Biogeochemistry. 108 (2012) 109–118.

[40] H.C. Hong, A. Mazumder, M.H. Wong, Y. Liang, Yield of trihalomethanes and haloacetic acids upon chlorinating algal cells, and its prediction via algal cellular biochemical composition, Water Res. 42 (2008) 4941–4948.

[41] J.D. Plummer, J.K. Edzwald, Effect of Ozone on Algae as Precursors for Trihalomethane and Haloacetic Acid Production, (2001).

[42] D.A. Reckhow, P.C. Singer, R.L. Malcolm, Chlorination of humic materials: byproduct formation and chemical interpretations, Environ. Sci. Technol. 24 (1990) 1655–1664.

[43] M.-L. Nguyen, P. Westerhoff, L. Baker, Q. Hu, M. Esparza-Soto, M. Sommerfeld, Characteristics and Reactivity of Algae-Produced Dissolved Organic Carbon, J. Environ. Eng. 131 (2005) 1574–1582.

[44] A.T. Chow, S. Gao, R.A. Dahlgren, Physical and chemical fractionation of dissolved organic matter and trihalomethane precursors: A review, J. Water Supply Res. Technol. - Aqua. 54 (2005).

[45] M. Kitis, T. Karanfil, J.E. Kilduff, A. Wigton, The reactivity of natural organic matter to disinfection by-products formation and its relation to specific ultraviolet absorbance., Water Sci. Technol. 43 (2001) 9–16.

[46] A.T. Chow, R.A. Dahlgren, Q. Zhang, P.K. Wong, Relationships between specific ultraviolet absorbance and trihalomethane precursors of different carbon sources, J. Water Supply Res. Technol. 57 (2008) 471–480.

[47] M.S. Fram, R. Fujii, B.A. Weishaar, L. J. Bergamaschi, G.A. Aiken, How DOC composition may explain the poor correlation between specific trihalomethane formation potential and specific UV absorbance, in: US Geol. Surv. Toxics Subst. Hydrol. Progr., 1990: pp. 423–430.

[48] R. Fabris, C.W.K. Chow, M. Drikas, B. Eikebrokk, Comparison of NOM character in selected Australian and Norwegian drinking waters, Water Res. 42 (2008) 4188–4196.

[49] H. Mash, P.K. Westerhoff, L.A. Baker, R.A. Nieman, M.-L. Nguyen, Dissolved organic matter in Arizona reservoirs: assessment of carbonaceous sources, Org. Geochem. 35 (2004) 831–843.

[50] A. Imai, T. Fukushima, K. Matsushige, Y.-H. Kim, K. Choi, Characterization of dissolved organic matter in effluents from wastewater treatment plants, Water Res. 36 (2002) 859–870.

[51] R.L. Malcolm, G.R. Aiken, E.C. Bowles, J.D. Malcolm, Isolation of fulvic and humic acids from the Suwannee River, in: R.C. Averett, J.A. Leenheer, D.M. McKnight, K.A. Thorn (Eds.), Humic Subst. Suwannee River, Georg. Interact. Prop. Propos. Struct., U.S. Geological survey, Federal centre, Denver, 1994: pp. 13–18.

[52] P. Westerhoff, H. Mash, Dissolved organic nitrogen in drinking water supplies: a review, J. Water Supply Res. Technol. 51 (2002) 415–448.

[53] J.L. Weishaar, G.R. Aiken, B.A. Bergamaschi, M.S. Fram, Roger Fujii, K. Mopper, Evaluation of Specific Ultraviolet Absorbance as an Indicator of the Chemical Composition and Reactivity of Dissolved Organic Carbon, Environ. Sci. Technol. 37 (2003) 4702–4708.

[54] N. Ates, M. Kitis, U. Yetis, Formation of chlorination by-products in waters with low SUVA-correlations with SUVA and differential UV spectroscopy, Water Res. 41 (2007) 4139–4148.

[55] M. Kitis, N.O. Yigita, B.I. Harmana, H. Muhammetoglu, A. Muhammetoglu, I.E. Karadirek, I. Demirel, T. Ozdenc, I. Palancic, Occurrence of Trihalomethanes in Chlorinated Groundwaters with Very Low Natural Organic Matter and Bromide Concentrations, Environ. Forensics. 11 (2010) 264–274.

[56] M. Doré, N. Merlet, B. Legube, J.P. Croue, Interactions Between Ozone, Halogens and Organic Compounds, Ozone Sci. Eng. 10 (1988) 153–172.
[57] WHO, Bromide in drinking-water: Background document for development of WHO Guidelines for Drinking-water Quality, 2009.
[58] G. Hua, D.A. Reckhow, Relationship between Brominated THMs, HAAs, and Total Organic Bromine during Drinking Water Chlorination, in: T. Karanfil, S.W. W. Krasner, Y. Xie (Eds.), Disinfect. By-Products Drink. Water, American Chemical Society, Washington, DC, 2008: pp. 109–123.
[59] K.M.S. Hansen, S. Willach, M.G. Antoniou, H. Mosbæk, H.-J. Albrechtsen, H.R. Andersen, Effect of pH on the formation of disinfection byproducts in swimming pool water - Is less THM better?, Water Res. 46 (2012) 6399–409.

CHAPTER 6

COMPARISON OF THMs AND HAAs FORMATION DURING ClO_2 AND Cl_2 TREATMENT

Chapter 6

Comparison of THMs and HAAs formation during ClO_2 and Cl_2 treatment

Abstract: Formation potential and speciation characteristics of two important groups of disinfection byproducts (DBPs), namely, trihalomethanes (THMs) and haloacetic acids (HAA$_S$), during Cl_2 and ClO_2 treatment of water samples collected from three different sources, namely, sea, river, and reservoir, were investigated with reference to key controlling parameters. Formation of inorganic DBPs such as chlorate and chlorite was evaluated. Dissolved organic carbon (DOC) and UV absorbance (UV_{254}) of the sea, river, and reservoir samples were 3.35±0.05, 3.12±0.05, and 3.23±0.05 mg/L and 0.062±0.01, 0.074±0.01, and 0.055±0.01, respectively. For Cl_2 and ClO_2 treatments, the respective formation potential of THMs and HAAs from the three water sources studied exhibited unidentical trend suggesting that higher THM formation was not necessarily associated with higher HAA formation. On chlorination, the concentrations of total HAAs formed were 9.8 µg/L (sea), 12.8 µg/L (river), and 20.6 µg/L (reservoir) and total THM yields were 38.3 µg/L (sea), 18.8 µg/L (river), and 21.5 µg/L (reservoir) for a Cl_2 dose of 1 mg/L and 30 min reaction time. The trend of formation of THMs and HAAs for ClO_2 treatment was similar to that for Cl_2 treatment. However, the amount of HAAs (3.5 µg/L (sea), 1.8 µg/L (river), and 1.9 µg/L (reservoir)) and THMs (not detected) formed during ClO_2 was much lower than that formed during chlorination. Regardless of source water type, di-HAAs were the most favored HAAs, followed by tri-HAAs with a small amount of mono-HAAs formed for both Cl_2 and ClO_2 treatment. Chlorination

yielded more THMs than HAAs, whereas it was reverse for chlorine dioxide treatment. Irrespective of treatment with ClO_2 or Cl_2, seawater samples showed the highest bromine incorporation percentage (BIP) in both THMs and HAAs followed by that for Palar river and open reservoir water samples. HAAs were found to be always associated with lower amount of BIP than THMs.

6.1 Introduction

Chlorination is widely used all over the world not only for disinfection of drinking water but also for biofouling control in industrial water utilities such as thermal power plants, refineries, petrochemical plants, and chemical processing plants. Depending on the availability and use, the requirement of water is fulfilled by various natural water sources such as seas, rivers, and lakes, or reservoirs. Disinfection of water from freshwater sources such as river and lake reservoir is carried out for providing safe drinking water, whereas seawater is disinfected during its use for various purposes such as desalination, aquaculture, cooling water, and swimming pool [1–4]. Two major classes of disinfection byproducts (DBPs) formed during chlorination, trihalomethanes (THMs) and haloacetic acids (HAAs), have been regulated by U.S. Environmental Protection Agency (USEPA) with maximum contaminant levels of 80 µg/L for THMs and 60 µg/L for HAAs [5]. To comply and to reduce the formation and discharge of disinfection byproducts (DBPs), some water utilities are looking for alternative chemical biocides [6,7] such as ozone, chloramines, trichlorocyanuric acid, and chlorine dioxide. Among these biocides, chlorine dioxide (ClO_2) has recently gained popularity as it generates significantly less THMs and HAAs [8] as compared to other oxidants. The level of developmental toxicity observed for the ClO_2 disinfected water samples was lower than that disinfected with Cl_2 in a recent study [6]. Many literature reports have also shown better effectiveness of chlorine dioxide at lower concentrations than that of Cl_2 as well as the lesser formation of DBPs during ClO_2 treatment as it does not undergo substitution reactions with natural organic matter (NOM) present in water [9,10]. Key factors controlling the formation of DBPs vary from one source to another because the source water character is governed by local geological and hydrological conditions [11]. Water samples from distinct sources, i.e., sea, river, and reservoir contain dissolved organic carbon (DOC) precursors that have originated from different biochemical processes. The intricacy of chemical characteristics and features of chlorination in seawater differ greatly from those of freshwaters namely, river water or reservoir water because of the oxidation of bromide present in seawater (~65 mg/L), thereby resulting in HOBr as the dominant oxidant species, unlike HOCl in fresh water. In case of water treatment with ClO_2, usually, up to 60% of the applied ClO_2 dose is reduced to chlorite ion, and 8-10% is converted to chlorate ion, and its formation is influenced by the presence of various organic and inorganic constituents in natural water [10,12–14]. Further, because the dominant mechanism of reaction of Cl_2 and ClO_2 with natural organic matters (NOMs) and other constituents of natural water are different, the type and level of the resultant DBPs are expected to be different. ClO_2 produces a lower level of organic by-products than chlorine [15]. Various factors like pH, temperature, oxidant concentration, NOM concentration, and precursor reactivity may affect the formation of DBPs. In addition, the presence of bromide greatly alters the speciation pattern and is also known to enhance the concentration of DBPs. To control the formation of various byproducts during oxidant treatment of source water, it is of great importance to know the characteristics of the precursor in the source water [4]. Apart from the toxicity concern of these DBPs in drinking water, discharge of the effluent containing these DBPs by the industrial water utilities also lead to the possibility of affecting human health through atmospheric volatilization and subsequent photolysis of brominated compound to reactive oxidants [16,17]. In case of water treatment with chlorine dioxide, decomposition of ClO_2 to form inorganic DBPs such as chlorite (ClO_2^-) and chlorate (ClO_3^-) is of much concern.

Despite intensive research conducted worldwide on DBPs formation, the studies based on real water have generally been limited to a small number of water sources [18]. To the best of our knowledge, this is the first report from India addressing the influence of different water source on the formation of THMs and HAAs during different oxidant treatments.

The objectives of the present study were (i) to evaluate the influence of water sources on the speciation and yield of THMs, HAAs, chlorate (ClO_3^-) and chlorite (ClO_2^-) as a result of Cl_2 and ClO_2 treatment (ii) to assess the effect of bromide level (high in seawater to moderate in coastal freshwater) on the shift of DBP species toward brominated analog and (iii) to compare the kinetics of formation and relative distribution of THMs and HAAs in Cl_2 and ClO_2 treated water under different treatment conditions.

6.2 Experimental conditions

In addition to the disinfection of drinking water, chlorine and chlorine dioxide treatment is an essential process in many water utilities such as biofouling control, swimming pool disinfection, aquaculture, food processing, etc. where the dose required and contact time are much different compared to that typically observed for drinking water. For example, for the titanium plate heat exchanger of a nuclear power plant at the study location (Prototype Fast breeder reactor, Kalpakkam, India), seawater is used for condenser cooling, the oxidant dose required is up to 25 mg/L, and the effluent is provisioned for dilution before discharge. Moreover, biocide concentration is very high at the point of its introduction which gets diluted on mixing with the bulk water subsequently. To have a comprehensive information on the DBPs formation behavior at different stoichiometry of disinfectant and dissolved organic content, it is essential to study a broad range of disinfectant dose in experimental studies as seen in previous literature [10,19,20]. Unlike temperate country, in a tropical country like India ambient water temperatures ranged between 20–25 °C during winter and 28–32 °C during summer/pre-monsoon in most of the mainland. Considering the fact that (1) temperature of the condenser effluent is typically 5-7 ^{0}C higher than the ambient temperature, (2) temperature of the water in reservoir with shallow depth goes up to 36-37^{0}C, (3) the water temperature during the daytime in the distribution pipe goes beyond 40^{0}C due to the exposure to direct sunlight; temperatures up to 40^{0}C was taken for the study. Water residence time in drinking water pipeline or overhead storage take often reaches 24 h. In cooling water system during maintenance or shut down water residence up to 24 h is also fairly practical. Similarly, disinfectant contact time of 24 h is quite usual for swimming pool and aquaculture pond. Experimental conditions were decided to include the above disinfection conditions in various water utilities. Water samples from seawater (SWR), Palar river (RVR) and open reservoir (RSR) were treated with the calculated amount of Cl_2 or ClO_2 working standard solutions to get initial oxidant doses of 0.1, 1, 3, 5, 10, and 25 mg/L to investigate the dose effect on DBPs formation. Residual oxidant concentration at various intervals was measured by the DPD-colorimetric method [10,21]. A portion of treated samples was withdrawn at different time intervals ranging from 30 to 1440 min for further extraction and analysis of THMs and HAAs. Samples were also drawn for chlorate and chlorite analysis. All the DBPs formation experiments were carried out at two different temperature 25^0C and 40^0C.

6.3 Results and Discussion

6.3.1 Water quality parameters of three source water

A summary of water quality parameters is presented in **Table 6. 1**. pH, temperature and DO of the three water-source were in the similar range, with SWR having the highest pH (8.21) and RVR having the lowest (7.36). DO of the SWR was marginally higher than those of RSR and RVR. However, chlorophyll-a values were not in the same trend, and the highest was observed for RSR (11.80 µg/L) followed by SWR (5.13 µg/L) and the lowest for RVR (1.06 µg/L). These chlorophyll-a values did not correlate with the DOC values of water, thus indicating the significant non-algal source of NOMs.

Table 6. 1 Summary of water quality parameters of source waters: Seawater (SWR), River water (RVR), Reservoir water (RSR)

Parameters	SWR	RVR	RSR
pH	8.21±0.1	7.36±0.1	7.66±0.1
Temp(^{0}C)	27.35±0.1	29.23±0.1	28.6±0.1
DO (mg/L)	6.26±0.04	5.50±0.04	5.61±0.04
EC (µs/m)	44370±68	492.20±22	657.00±19
Chl-a (µg/L)	5.13±0.1	1.06±0.1	11.80±0.1
NO_3 (µM)	0.55±0.03	13.81±0.06	2.66±0.1
TN (µM)	3.30±0.1	15.62±0.81	17.64±0.78
Br^- (mg/L)	67.23±2.1	0.88±0.12	1.34±0.16
DOC (mg/L)	3.35±0.05	3.12±0.05	3.23±0.05
UVA_{254} (cm^{-1})	0.062±0.01	0.074±0.01	0.055±0.01
$SUVA_{254}$ (L mg^{-1} m^{-1})	1.85±0.1	2.36±0.1	1.70±0.1

EC: Electrical conductivity, DO: dissolved Oxygen, Chl-a: Chlorophyll-a, TN: Total nitrogen, DOC: Dissolved organic carbon.

Although the DOC value was the lowest for RVR, it had the highest UV_{254} value (0.074 cm^{-1}) as compared to 0.062 and 0.055 cm^{-1} for SWR and RSR respectively. The nutrient richness of the river water was reflected by the presence of high nitrate and total nitrogen content. The NO_3^- value for SWR was 0.055 µM and was the lowest among the three water sources. Bromide content in the water is a key influencing parameter that affects the DBPs species distribution. Estimated bromide content of the SWR was 67.33±2.1 mg/L, which was much higher than those of RSR (1.34±0.16 mg/L) and RVR (0.88±0.12 mg/L).

6.3.2 Formation, distribution, and speciation of HAAs and THMs

The parameters for identification and quantification of organic and inorganic DBPs as well as the analytical performance of operating conditions are provided in **Table 6. 2**. Unlike chlorine, chlorine dioxide does not generally take part in the direct substitution reaction with natural organic matter present in the water. The possible aqueous chemistry of ClO_2 depicting the possible pathways for DBP formation is outlined below in eqs.6.1- 6.4 [20,22,23]

$$\mathrm{ClO_2} \xrightarrow{+e^-} \mathrm{ClO_2^-} \xrightarrow{+2e^-} \mathbf{ClO^-} \xrightarrow{+2e^-} \mathrm{Cl^-} \qquad (6.1)$$

$$\mathrm{ClO^-} + \mathrm{Br^-} + \mathrm{H_2O} \rightarrow \mathbf{HOBr}\ (\text{in the presence of bromide}) \qquad (6.2)$$

$$ClO_2 + 2Br^- \xrightarrow{light} Br_2 + \mathrm{H_2O} \rightarrow \boldsymbol{HOBr} \qquad (6.3)$$

$$HOCl(orOCl^-)/HOBr(or\ OBr^-) + NOMs \rightarrow Cl(orBr) - THMs\ and\ HAAs \quad (6.4)$$

Figure 6. 1 illustrates the concentration of total HAAs (THAAs) and total THMs (TTHMs) formed due to Cl_2 and ClO_2 treatments of SWR, RWR, and RSR samples after 30 min and 24 h, at temperatures of 25^0C and 40^0C and doses of 1 and 25 mg/L.

Table 6. 2 Chemical formula and analytical parameters for THMs, HAAs, Chlorate and Chlorite

DBPs name & chemical formula	RT (min)	R^2 (n=7)	MDL (µg/L)	Avg. Recovery (%)	% (Avg) RSD	Instrument Conditions
Monochloroaceticacid ($ClCH_2COOH$)	6.34±0.04	0.9920	0.05	103.2	10.22	Gas Chromatograph Detector: electron capture detector Injector temp.: 150^0C Detector temp: 270^0C Split ratio: 1:5 N_2 flow: 1ml/min Temp programme: 35^0C -15min-75^0C@5^0C-10min-100^0C@5^0C-5 min-135^0C@5^0C-2 min-200^0C@25^0C-2 min
Monobromoacetic acid ($BrCH_2COOH$)	9.81±0.04	0.9980	0.01	103.4	10.5	
Dichloroacetic acid ($Cl_2CHCOOH$)	10.62±0.07	0.9976	0001	98.9	8.96	
Trichloroacetic acid (Cl_3CCOOH)	17.86±0.07	0.9959	0.01	96.3	9.69	
Bromocholo acetic acid (ClBrCHCOOH	18.02±0.09	0.9856	0.01	100.6	7.89	
Dibromo acetic acid ($Br_2CHCOOH$)	22.65±0.09	0.9889	0.01	98.63	7.66	
Bromodichloroacetic acid ($Cl_2BrCCOOH$)	23.11±0.09	0.9898	0.01	93.69	9.12	
Dibromochloroacetic acid ($ClBr_2CCOOH$)	29.01±0.10	0.9886	0.05	92.69	11.22	
Tribromo acetic acid (Br_3CCOOH)	36.09±0.10	0.9869	0.1	91.25	12.36	
Chloroform ($CHCl_3$)	3.17±0.05	0.9997	0.10	99.9	10.2	N_2 flow: 1.5 ml/min Temp programme: 30^0C -10min-41^0C@3^0C-6min-1 81^0C@5^0C-180^0C@25^0C-6 min (other GC condition same as above)
Dichlorobromomethane ($CHCl_2Br$)	4.91±0.05	0.9996	0.02	100.2	4.32	
Chlorodibromomethane ($CHClBr_2$)	8.811±0.05	0.9996	0.02	101.2	3.16	
Bromoform ($CHBr_3$)	15.30±0.1	0.9994	0.05	102.6	8.96	
Chlorite ClO_2^-	5.23	0.9988	5.0	95.66	2.12	Ion Chromatograph, Dionex AS19, AG19 column, eluent: 20 mM KOH; flow: 1ml/min, conductivity detection
Chlorate ClO_3^-	9.41	0.9959	5.0	96.52	2.22	

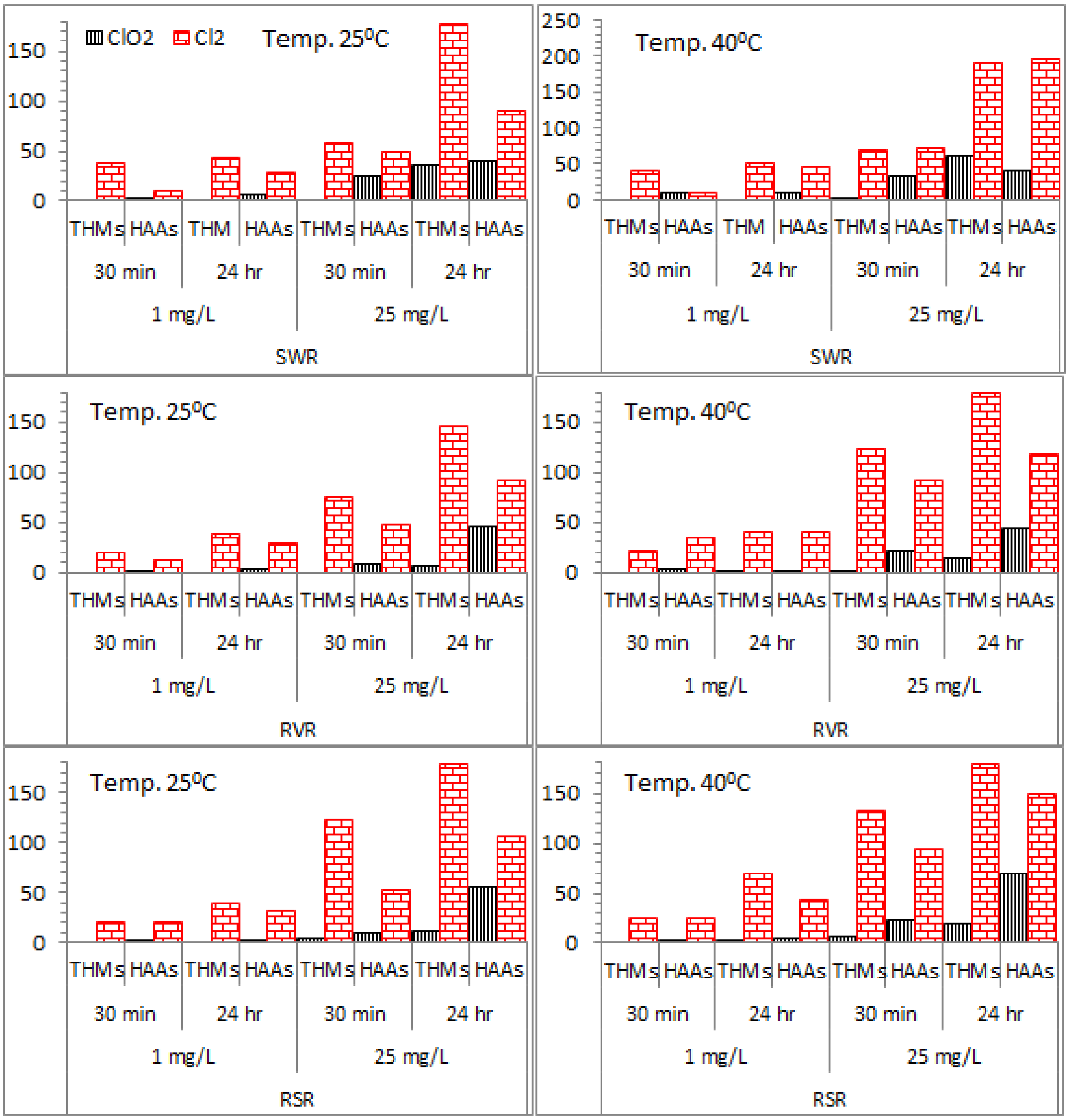


Figure 6. 1 Comparison of DBPs (THMs and HAAs) formation potential of three source water during ClO2 and Cl2 treatment; ClO2/Cl2: 1 and 25 mg/L, Time: 30 min and 24 h, Temp: 250C and 400C (SWR: seawater, RVR: River water, RSR: Reservoir water)

The results up to 24 h contact time showed that the order of DBPs formation potential on chlorination was RSR > SWR > RVR except for the lower chlorine dose where oxidant concentration is rate limiting. On chlorination, at contact time of 30 min, the yield of THAAs varied from 9.8 µg/L (SWR), 12.8 µg/L (RVR), and 20.6 µg/L (RSR) for a chlorine dose of 1 mg/L to 49.1 µg/L(SWR), 46.7 µg/L (RVR), and 51.6 µg/L

(RSR) for a Cl_2 dose of 25 mg/L. Whereas, the TTHM yield varied from 38.3 µg/L (SWR), 18.8 µg/L(RVR), 21.5 µg/L (RSR) to 59.1 µg/L(SWR), 76.1 µg/L (RVR), and 122.8 µg/L (RSR) for the same conditions. This observation indicated that all three raw water sources are significantly susceptible to the formation of both the DBPs group. For other chlorine doses studied (3, 5, and 10 mg/L), the concentration of TTHMs and THAAs concentration gradually increased on increasing the chlorine concentration though it did not increase linearly. Only approximately 10-25% increase in THMs and HAAs values were observed on increasing the chlorine dose more than double from 10 to 25 mg/L. Similar observations for raw water of Dez River, Iran have been reported [24]. On the other hand, on increasing the reaction time from 30 min to 24 h, two- to three-fold increase in the concentration of TTHMs and THAAs was noticed. The concentration of THAAs and TTHMs increased from 49.1 and 59.1, 46.7 and 76.1 and 51.6 and 122.8 µg/L to 90.0 and 177.8, 91.5 and 146.3 and 106.5 and 179.1µg/L on increasing the contact time from 30 min to 24 h (25 mg/L Cl_2) for SWR, RVR and RSR respectively. Generally, DBPs continue to form as long as residual oxidant and precursor are present and the rate of the formation may vary greatly with the properties of organic matter. Our results showed that ClO_2 followed an initial rapid decay reducing the residual to 0.6-0.7 mg/L within 5 min for 1 mg/L of the applied dose. ClO_2 residuals available at 24 h were 0.25 (SWR), 0.40 (RVR), 0.25 (RSR) mg/L for 1 mg/L applied dose at 25^0C and 0.15 (SWR), 0.20 (RVR), 0.15 (RSR) mg/L at 40^0C. The observations were similar for other disinfectant doses studied. Residuals remained for the highest doses studied, i.e., 25 mg/L after 24 h contact time at 25^0C were 7.8 (SWR), 9.2 (RVR) and 8.2 (RSR) mg/L. Decay trend for the Cl_2 residual during different experimental conditions was alike to that of ClO_2.

However, the decay rate was more rapid, and no residual remained after 24 h contact time for 1, and 3 mg/L applied chlorine dose. At 25^0C; 6.9, 7.6, and 7.1 mg/L of residual were available for the 25 mg/L of the Cl_2 dose after 24 h for SWR, RVR, and RSR respectively. In the present study, the level of both the DBPs increased significantly on increasing reaction time, although the rate became much slower after 30 min. Our observations are similar to those given in previous reports [25,26] which support the fact that chlorine first reacts with the active group quickly, thus leading to the rapid initial formation of DBPs. As the reaction time progressed, both residual oxidant and reactive precursor decreased which lead to slowing down of the DBP formation rate. The trend observed on the formation of TTHMs and THAAs with regards to oxidant dose and time was similar for Cl_2 and ClO_2 treatment; however, the level of formation of both HAAs and THMs was much lower than that formed due to chlorination. THMs were not detected for SWR and RVR samples even up to 25 mg/L of ClO_2 for samples drawn after 30 min contact time and varied from 1.0 to 3.7 µg/L for the RSR water sample under similar conditions. However, on increasing the reaction time up to 24 h, 35.7 µg/L (SWR), 5.90 µg/L (RVR), and 12.1 µg/L (RSR) of TTHMs were observed. Similarly, THAAs yield were 3.5 µg/L (SWR), 1.8 µg/L(RVR), and 1.9 µg/L (RSR) and 25.7 µg/L (SWR), 8.6 µg/L (RVR), and 9.9 µg/L (RSR) for 1 and 25 mg/L ClO_2 concentrations respectively for 30 min of contact time, which increased to 39.7 µg/L (SWR), 45.0 µg/L(RVR), and 56.2 µg/L (RSR) for 24 h with 25 mg/L ClO_2. TTHM and THAA values observed in the present study remained below the USEPA minimum contaminant level (MCL) of 60 µg/L for up to 25 mg/L dose of ClO_2. However, as high as nearly 5000 µg/L HAAs has been reported for the chlorine dioxide treatment of natural seawater with a 30 mg/L of ClO_2

for a contact time of 72 h [20]. The order of DBP (sum of TTHM and THAA) formation potential for 30 min reaction time of ClO_2 with different source water was SWR > RSR > RVR whereas it was RSR > SWR > RVR for chlorination (**Figure 6. 1**). Precursor reactivity for RVR and RSR was comparatively slower and steady. Time dependence of HAAs formation was observed to be more pronounced for ClO_2 treatment with RSR and RVR samples than that with SWR samples, thus indicating different precursor properties of seawater and freshwater toward its reactivity with Cl_2 and ClO_2. Typical contrasting features of the dissolved organic matter are that seawater is enriched in N, H, and S compared to that of terrigenous organic matter present in the river [27]. The dissolved organic matter present in the riverine system has a greater proportion of $COOH/COO^-$ and more aromatic structures than that in the marine water [28]. Cl_2 and ClO_2 react with the dissolved organic matter through different pathways, and the NOM reactivity is significantly influenced by its physicochemical properties such as molecular weight, aromaticity, elemental composition, and presence of functional groups [29]. **Figure 6. 1** also shows the total HAAs and THMs formed at two different temperatures, i.e., 25^0C and 40^0C. Generally, an increase in temperature accelerates the reaction rate. However, high temperature also increases the decomposition of thermally unstable THMs and HAAs, particularly the bromine-containing species [30] thus, the outcome is the combined effect of formation and decomposition. For example, a significant amount of THMs at elevated temperature through hydrolysis and the decreasing order of the decomposition is $CHBrCl_2 > CHBr_2Cl > CHBr_3 > CHCl_3$, as reported by Zhang et al. (2015) [31]. Results of the present study under all studied conditions showed a net positive effect, that is, a higher amount of THMs and HAAs were observed on increasing the temperature from 25^0C to 40^0C for chlorine treatment. In contrast, a decrease in HAAs values during chlorination of Jin Lan reservoir water, China was observed by Hong et al. (2013) [32] when water temperature was increased from 20^0C to 30^0 C. In general, chlorine dioxide was found to be more sensitive to temperature increase than chlorine for the formation of HAAs and THMs. Among the three studied water sources, the propensity of total DBPs yield was RSR > SWR > RVR on increasing the temperature. For low-dose chlorination at 1 mg/L with 24 h contact time, where precursor is a not limiting factor for DBPs formation, on increasing the temperature from 25^0C to 40^0C, THAA yield increased by 60%, 40%, and 38% and that of TTHMs increased by 18%, 7%, and 70% for SWR, RVR, and RSR water samples respectively. The above increase in the yield of the individual class of DBPs corresponds to 57.3%, 35%, and 21.4% increase in total amount of DBPs (combined THAAs and TTHMs) for RSR, SWR, and RVR samples respectively. Under similar conditions, treatment with ClO_2 yielded a fewer amount of THAAs which ranged between 2.0 and 6.8 µg/L at 25^0C to 4 and 10.9 µg/L at 40^0C and THMs (0.6 µg/L) were detected only for RSR samples at 40^0C. At an oxidant dose of 0.5-1.5 mg/L which is generally adopted for biofouling control in cooling water system of power plant[33], often the oxidant is the rate-limiting factor. Under such a condition, both THMs and HAAs followed the initial rapid formation for up to 30 min and subsequent slow, prolonged formation, thereby contributing only a small amount to the total DBPs yield (**Figure 6. 2**). Once-through cooling is normally adopted by thermal power plant when seawater is used for condenser cooling and cooling water residence time from the point of chlorination to discharge is approximately 5-10 min. In such cases, it appears from our study that, expected discharge level of both the DBP groups in the cooling water discharge will always be less than the maximum contaminant guideline values stipulated by USEPA. **Figure 6. 3** shows the relative contributions of TTHMs and THAAs under different chlorination and chlorine dioxide treatment conditions. It clearly showed that TTHM was the major fraction in the case of chlorination under all experimental conditions, whereas, THAAs accounted for more than 90% of combined HAAs and THMs formed during treatment of water by chlorine dioxide. This indicated that the mechanism of precursor reactivity towards Cl_2 and ClO_2 follows different pathways, and selectivity behavior of the reaction site of NOMs was also not the same for Cl_2 and ClO_2. Higher temperature and increase in oxidant concentration resulted in a decrease in THAA/TTHM ratio for chlorine dioxide, whereas it was affected to a lesser extent for chlorination. Among three water sources, seawater demonstrated the lowest HAAs to THMs ratio followed by RSR and RVR samples.

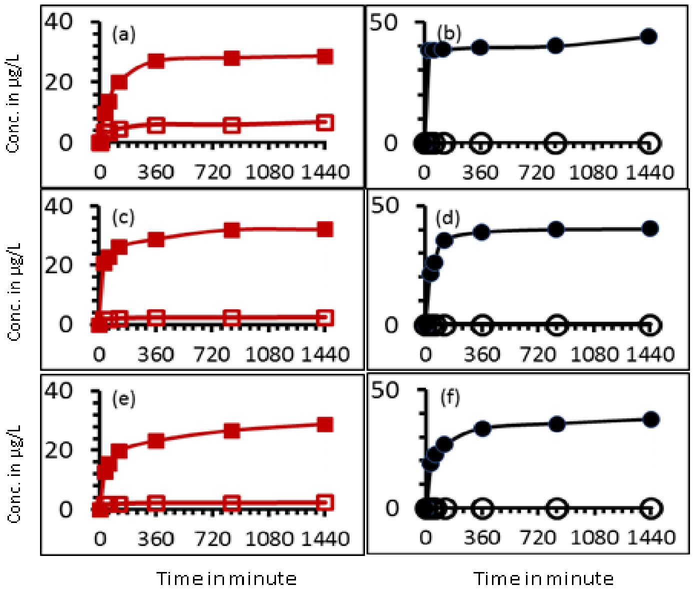


Figure 6. 2 Time course formation of total THMs (b, d, f) and total HAAs (a, c, e) on treatment of raw water with 1mg/L of Cl_2 (solid marker point) and ClO_2 (hollow marker point); SWR: Seawater (a) and (b), RVR: River water (c) and (d), RSR: Reservoir water (e) and (f).

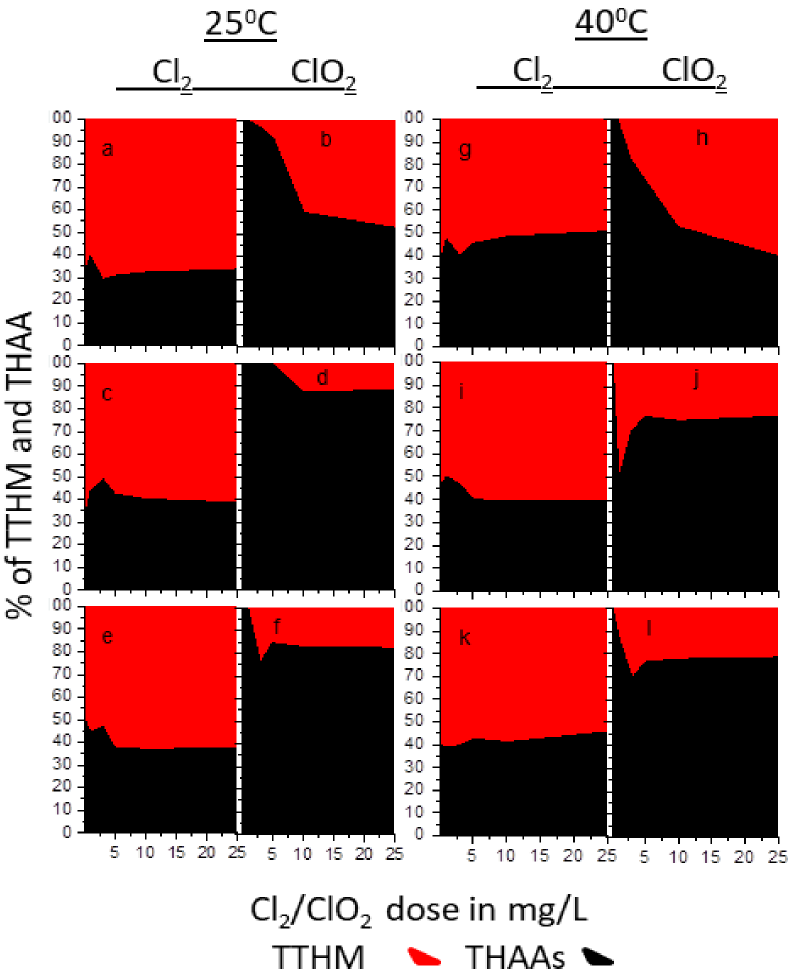


Figure 6. 3 Comparison of THM and HAA fraction on treatment of water with 1-25 mg/L of Cl_2 and ClO_2 after 24 h at 25^0C and 40^0C; a, b,g,h: Seawater; c,d,I,j: River water; e, f,k,l: Reservoir water.

The effect of Cl_2 and ClO_2 dose on the formation of THMs and HAAs under different conditions is illustrated in **Figure 6. 4**. THMs and HAAs formation showed an increasing trend with increasing oxidant concentration. However, the decrease was 7-10 times in the DBPs yield per mg/L of Cl_2 as the Cl_2 concentration increased from 0.1 to 25 mg/L. When the Cl_2 dose increased from 0.1 to 25 mg/L, [THAAs] per mg/L of Cl_2 decreased from 29.1, 22.0, and 41.1 µg/(mg/L) to 3.6, 3.7, and 4.2 µg/(mg/L) for SWR, RVR, and RSR respectively. A similar trend was observed for TTHMs,

[TTHM] per mg/L of Cl_2 decreased from 61.0, 48.0, and 41.0 µg/(mg/L) to 7.1, 5.9, and 7.1 µg/(mg/L) for SWR, RVR, and RSR respectively. For chlorine dioxide, THAAs yield per unit concentration of ClO_2 showed a similar trend with a much lower magnitude. THMs were not detected for a lower ClO_2 dose, and its yield per mg/L of ClO_2 was found to increase with increasing dose for all the three water sources.

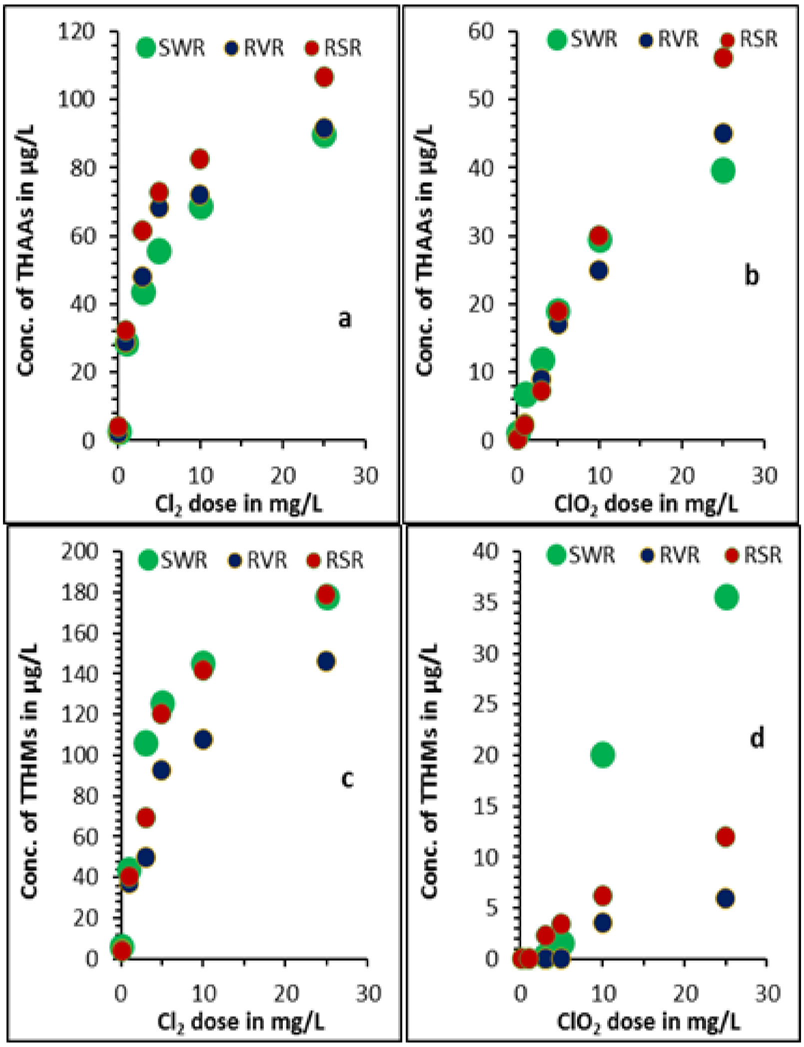


Figure 6. 4 Influence of oxidant concentration on the formation of THMs (a,b) and THAAs (c, d) for SWR, RVR, and RSR (contact time of 24 h at 25^{0}C)

In addition to the total DBP level, species distribution is of critical concern because brominated analogs are usually more cytotoxic and genotoxic and potentially more carcinogenic than their chlorinated analog [34–36]. For example, monobromoacetic acid is approximately 70 times more cytotoxic and 23.5 times more genotoxic than monochloroacetic acid [37]. Percentage contribution of nine HAAs and four THMs was evaluated during Cl_2 and ClO_2 treatments of seawater (SWR) and freshwater (RVR and RSR). Bromide content of the SWR sample was 67.23±2.1 mg/L, whereas it was 0.88±0.12 and 1.34±0.16 mg/L for RVR and RSR samples respectively (**Table 6. 1**). Due to the small variation in the bromide level in RVR and RSR samples, species distribution of HAAs and THMs was not of much difference for RVR and RSR samples. Hence, THMs and HAAs distribution in RVR and RSR samples were presented as a combined one. The box plot, as shown in **Figure 6. 5 (a)** and **(b),** describes the overall distribution of nine HAAs in seawater and **Figure 6. 5 (c)** and **(d)** that of for freshwater upon treatment with 1-25 mg/L of oxidant after a contact time of 30 min and 24 h. The pattern of HAAs species distribution was distinct for seawater and fresh water. The HAAs species distribution was also found to be greatly influenced by the nature of oxidant. For seawater chlorination, DBAA (dibromoacetic acid) and TBAA (tribromoacetic acid) constituted the major fraction of total HAAs followed by DCAA (dichloroacetic acid) and TCAA (trichloroacetic acid). The predominance of dibromoacetic acids and tribromoacetic acids as observed in the present study was in agreement with previously reported data [2,17]. Concentrations of mixed chlorobromo-HAA species were very less, and MCAA (monochloroacetic acid) was not detected in seawater samples in most of the experimental conditions. On the other hand, the trend is not analogous to ClO_2 treatment, and DBAA was observed to be the single dominant fraction contributing to 65-90% of total HAAs during ClO_2 treatment of seawater. Dihalogenated HAAs followed by trihalogenated HAAs were usually observed to be the dominant HAAs species during ClO_2 treatment [7], and in seawater, DBAA was reported to be the most predominant HAAs [38].

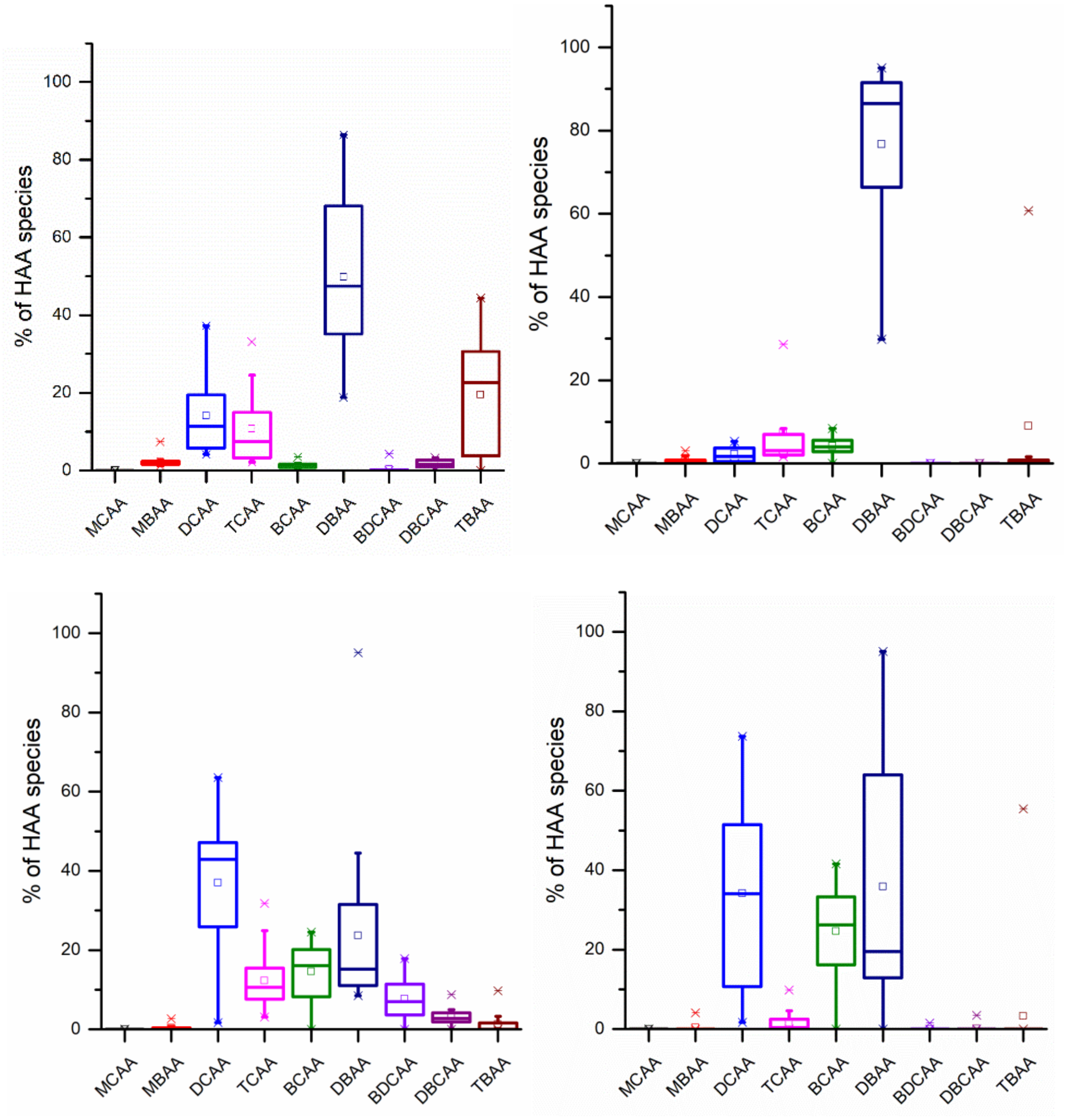


Figure 6. 5 Distribution of nine HAA species in freshwater (River and reservoir) treated with (a) Cl_2: dose 1-25 mg/L; time 30 min-24 h and (b) ClO_2: dose 1-25 mg/L; time 30 min-24 h and in seawater treated with (c) Cl_2: dose 1-25 mg/L; time 30 min-24 h (d) ClO_2: dose 1-25 mg/L; time 30 min-24 h.

Concentration of other HAAs was very less and followed the order TCAA > BCAA > DCAA > TBAA > MBAA. MCAA, BDCAA (bromodichloroacetic acid) and DBCAA (dibromochloroacetic acid) were not detected on chlorine dioxide treatment of seawater. For freshwater, a significant amount of mixed bromochloro-HAAs was observed after chlorination (**Figure 6. 5 (a)** and **(b)**). This was due to the coexistence of both $HOBr(OBr^-)$ and $HOCl(OCl^-)$ as reactive oxidant species because of the presence of an appreciable amount of bromide in the freshwater samples. DCAA was dominant and contributed to approximately 50% of total HAAs, followed by DBAA, BCAA, TCAA, and BDCAA. Changing the nature of oxidant from Cl_2 to ClO_2 also had a profound effect on the species distribution in freshwater. Unlike that observed for chlorine treatment, DBAA, DCAA, BCAA, and a small amount of TCAA together contributed to more than 90% of the total HAAs on chlorine dioxide treatment of freshwater. Since there is marked difference in characteristics of NOMs and presence of bromide in seawater, there could be difference in the DBP formation chemistry that could lead to a DBPs distribution [39] in SWR different from that in freshwater (RVR and RSR) as described in **Figure 6. 5 (a)** and **(b)**. However, in general, it can be inferred from the results that because of their relative stability di-HAAs are more readily formed than tri-HAAs with a significantly lower amount of mono-HAAs for any type of source water. Further, as the origin of NOMs and the biogeochemical processes involved may be specific to the water source, the mechanism that leads to HAAs formation in distinct water sources may be location specific. Results of the formation kinetics also showed that DBAA and DCAA were the first to be detected among all the HAAs species. Although the bromide level of the RVR and RSR varied between 0.5 and 1.1 mg/L, a considerable amount of brominated-HAAs was formed, and DBAA was even the highest fraction for chlorine dioxide treatment of freshwater. This indicated that reaction of ClO_2 induced bromide containing intermediate oxidant species with the organic precursor as the principal pathway of HAAs formation during chlorine dioxide treatment (eqs. 6.3 and 6.4).

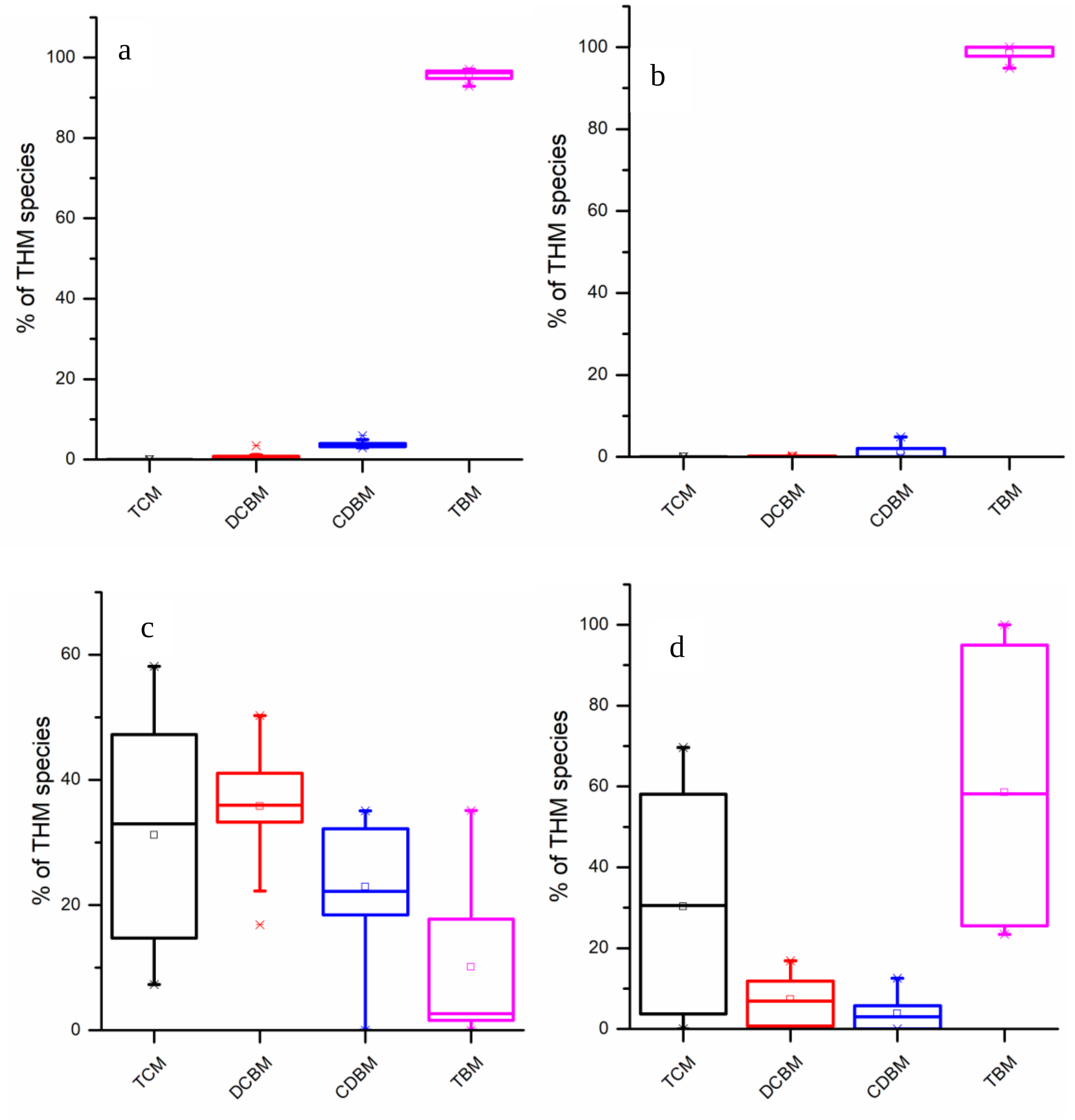


Figure 6. 6 Distribution of four THM species in seawater treated with (a) Cl_2: dose 1-25 mg/L; time 30 min-24 h and (b) ClO_2: dose 1-25 mg/L; time 30 min-24 h and freshwater treated with (c) Cl_2: dose 1-25 mg/L ; time 30 min-24 h and (d) ClO_2: dose 1-25 mg/L; time 30 min-24 h

With regard to THMs species distribution in seawater, bromoform was observed to be the single dominant species constituting approximately 90-98% of the total THMs for both Cl_2 and ClO_2 treatment (**Figure 6 (a)** and **(b)** which is in agreement with previously reported results [2,20]. However, in freshwater (RVR and RSR) it was more widely distributed among all the four species **(Figure 6. 6 (c)** and **(d**). In freshwater, the order of distribution was TCM (trichloromethane)~DCBM (dibromochloromethane) > CDBM (chlorodibromomethane) > TBM (tribromomethane) for chlorination and TBM > TCM > DCBM > CDBM for chlorine dioxide. The distribution of THMs between chloro- and bromo- analogs primarily dependent on the concentration of bromide in the raw water. For instance, in a study carried out by Zhang et al. (2000) [7] with the Suwannee River fulvic acid with 0.1 mg/L bromide resulted in the THMs distribution order as BDCM>TBM>TCM>DBCM during ClO_2 treatment. As expected, the presence of bromide affected the distribution of both the DBPs classes considerably. **Figure 6. 7 (a), (b)** and **(c)** illustrate the significance of bromide content in the raw water on the percentage of bromine incorporation (BIP) in RVR, SWR, and RSR respectively. High BIP was observed for TTHMs (~98%) and HAAs (60-90%) and values were similar for both Cl_2 and ClO_2 treatment of seawater. However, for freshwater treated with ClO_2, higher bromine incorporation into THMs followed by HAAs was observed than that observed for freshwater treated with chlorine. Increased bromide incorporation on ClO_2 treatment of the source water having moderate bromide concentration may be a critical factor to be considered when shifting the water treatment from chlorine to chlorine dioxide. The order of BIP in THMs and HAAs for the three water sources was SWR > RVR > RSR regardless of whether water was treated with ClO_2 or Cl_2. BIP values for HAAs were always found to be lower than those for THMs. The present study also demonstrated that THMs have a greater tendency for bromine incorporation on increasing the bromide level. To verify the same, the RVR sample was chlorinated in the presence of excess bromide to chlorine molar ratio (molar $Br^-/HOCl = 1.5$).

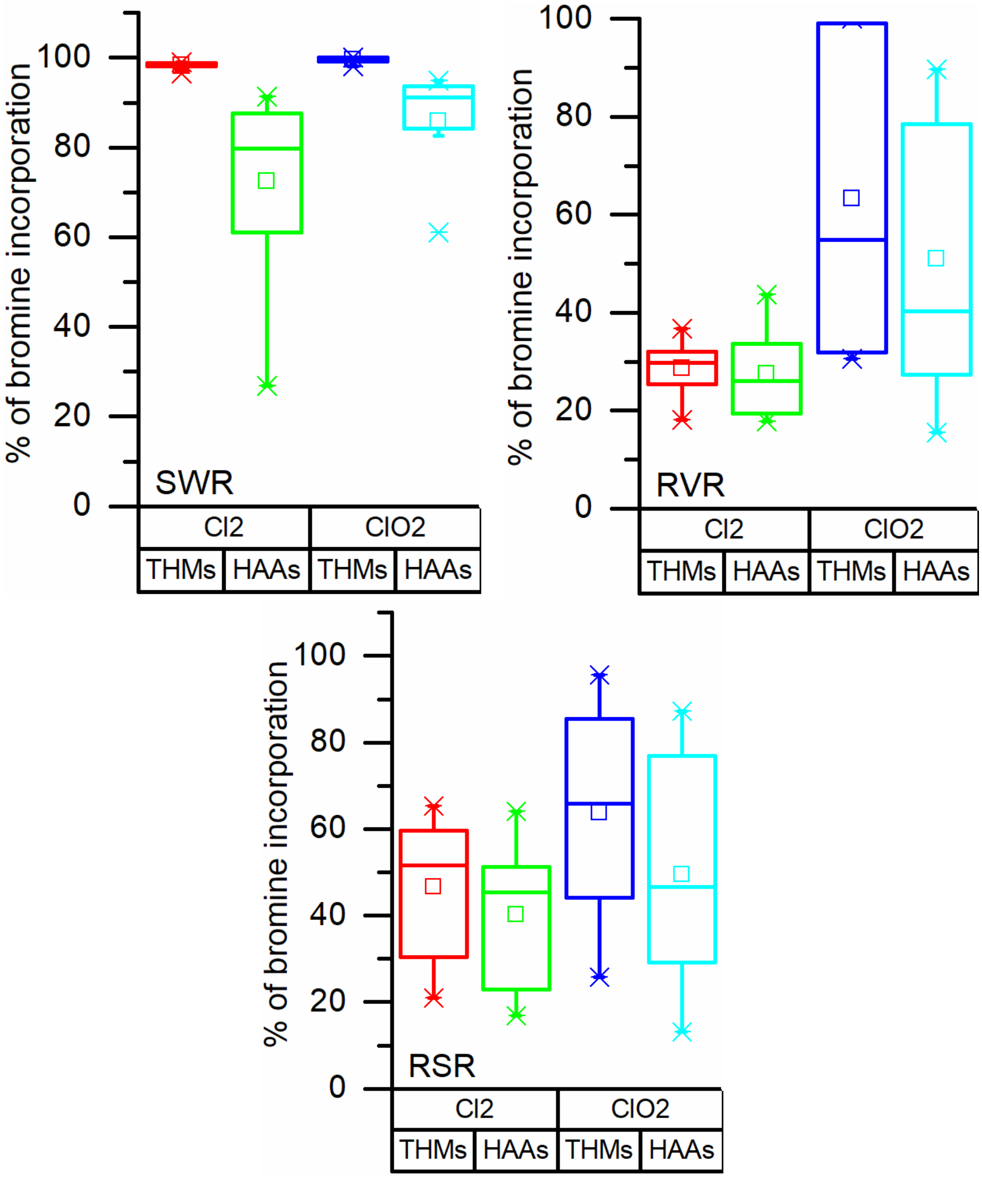


Figure 6. 7 Box plot of bromine incorporation percentage into THMs and HAAs for chlorination and chlorine dioxide treatment under all experimental conditions (Cl_2: dose 1-25 mg/L; ClO_2: dose 1-25 mg/L; time 30 min-24 h; temp:25^0C) for SWR(a), RVR(b), RSR(c).

The distribution variations in HAAs and THMs species are presented in **Figure 6. 8**. It was observed that the species distribution shifted from the dominance of dichloro- and trichloro- HAAs on chlorination in the absence of excess bromide to dibromo and tribromo-HAAs in the presence of excess bromide. Although the species shift to bromo derivative of HAAs was evident, a significant amount of chloro or mixed HAAs was also present (**Figure 6. 8 (a)** and **(b))**. However, in the case of THMs, there was a complete shift to 98% of TBM in the presence of excess bromide from 10%-TCM, 48%-DCBM, 33%-CDBM and 7%-TBM **Figure 6. 8 (c)** and **(d)**. The total yield of DBPs was also associated with 108.5% increase in TTHMs (µM) and 69.9 % increase in HAAs (µM) (**Figure 6. 9**) because of the powerful substitution ability and high molecular weight of bromine [40,41].

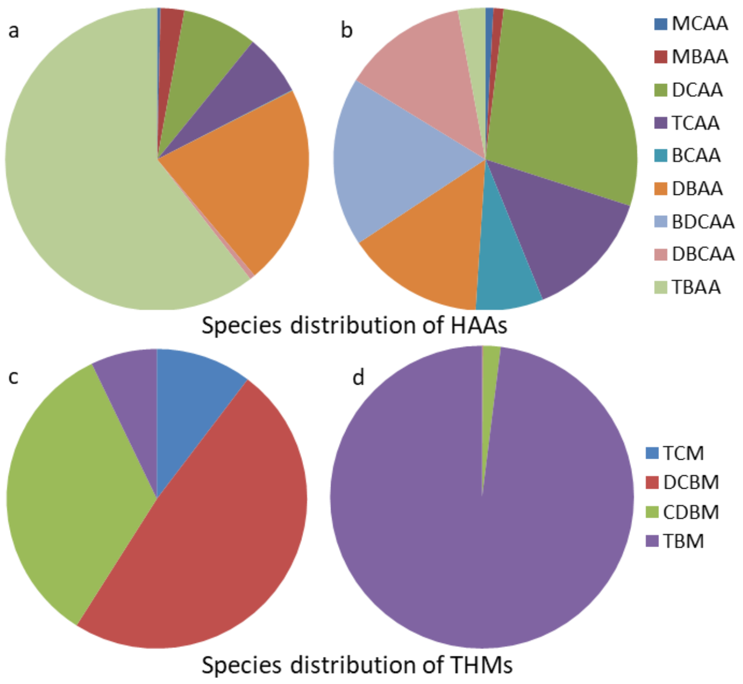


Figure 6. 8 Pie -chart showing the change in species distribution of HAAs and THMs on chlorination of natural freshwater and after addition of excess bromide (a, c: natural water; b, d: in the presence of excess bromide)

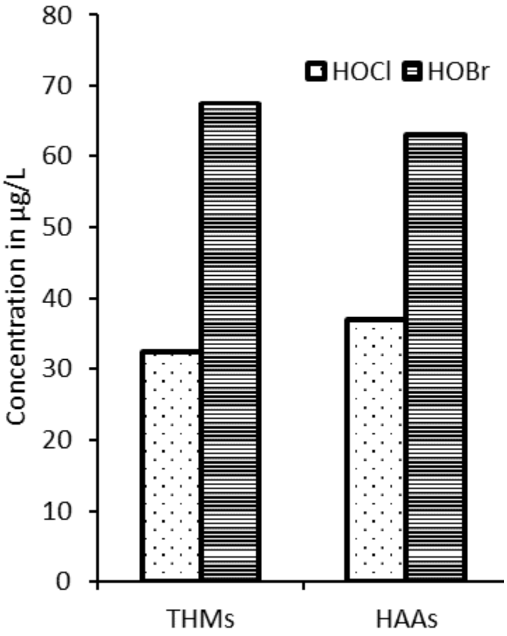


Figure 6. 9 Enhancement of DBPs (THMS and HAAs) yield on chlorination of freshwater in the presence of excess bromide.

6.3.3 Formation and distribution of ClO_2^- and ClO_3^-

ClO_2^- and ClO_3^- are the DBPs of significant concern that are formed during the chlorine dioxide treatment of water. Their concentration in the treated natural water is dependent on the applied ClO_2 dose and the nature of dissolved organic matter in the source water [12,21]. In aqueous solution, neutral and alkaline conditions favor the formation of acidic radicals (eq. 5.5), and under high pH conditions, ClO_2 tends to react by exchanging an electron to produce chlorite ion (eq. 5.6).

$$\mathrm{ClO_2} + 2\mathrm{OH}^- \leftrightarrow \mathbf{ClO_2^-} + \mathbf{ClO_3^-} + \mathrm{H_2O} \qquad (6.5)$$

$$\mathrm{ClO_2} + \mathrm{e}^- \leftrightarrow \mathbf{ClO_2^-} \qquad (6.6)$$

Table 6. 3 presents the summary of ClO_2^- and ClO_3^- formed in the different source water at different disinfectants doses. Chlorate was detected in the untreated RSR (51 µg/L) and RVR (62µg/L) water samples. Chlorite was not detected in any of the untreated source water samples. On treatment with deionized water, it was found that

chlorine dioxide was disproportionate to 15-39% chlorate and 0-12% chlorite for the dose ranging from 1 to 25 mg/L and contact time from 30 min to 24 h. The conversion of ClO_2 to ClO_2^- was maximum at 60 min and after that, it decreased marginally to about 2% during a 24 h period for all the water samples. The disproportion of ClO_2 was also observed to be affected by the nature of the water source (**Figure 6. 10**).

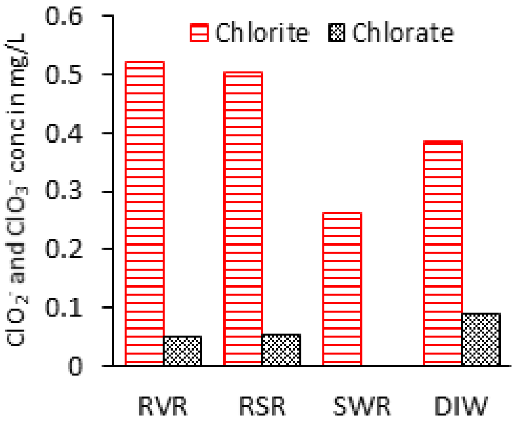


Figure 6. 10 Distribution of chl;orite and chlorate in Seawater (SWR), River water (RVR), Reservoir water (RSR) and Deionised water (DIW) after contact time of 30 min and 1 mg/L chlorine dioxide.

The ClO_2^- level varied from 15% to 31%, 36% to 52% and 31 to 62% of the applied ClO_2 for SWR, RSR, and RVR water samples respectively for 1-25 mg/L of ClO_2. The level of chlorite ion formed in the seawater was lower than that in freshwater (RSR and RVR) samples, which may be due to the presence of very high chloride content (~19,000 mg/L) in the seawater. Chlorate remained undetectable in the SWR sample, and it varied between 5% and 13% and 3% and 8% of the applied chlorine dioxide concentration for the RVR and RSR samples respectively. The above results indicated that a significant amount of chlorite and chlorate would be introduced to the finished water during chlorine dioxide treatment of natural water. The level of chlorite in treated water increased as the chlorine dioxide dose increased, however, up to 50%

reduction in the conversion of ClO_2 to ClO_2^- was observed on increasing the dose from 1 to 25 mg/L. A substantial amount of chlorate was present ranging from 19% to 28% in all the chlorinated natural water samples (**Table 6. 3**). However, its presence up to 31-37% in the feed NaOCl confirms that it was majorly because of the high level of chlorate present in the hypochlorite solution used for chlorination experiments. On analysis, it was found that chlorate content in the NaOCl feed solution was 10200 mg/L (analyzed after 10,000 dilutions). Thus, the presence of chlorate in the chlorinated water was the direct result of the contamination in the hypochlorite solution rather than the conversion of OCl^-. During manufacturing and storage, hypochlorite was disproportionate to produce chlorate as per eq. 6.7and 6.8 and resulted in a significant amount of chlorate in the hypochlorite solution [42,43]. However, most large-scale utilities use chlorine gas for chlorination of natural water and chlorate has not been detected in the finished water [43,44].

$$2ClO^- \xrightarrow{slow} Cl^- + ClO_2^- \tag{6.7}$$

$$ClO^- + ClO_2^- \xrightarrow{fast} Cl^- + ClO_3^- \tag{6.8}$$

In the present study, chlorite was detected neither in the hypochlorite solution nor in any of the chlorine disinfected source water samples. At higher temperature (40^0C), the level of both the chlorite and chlorate decreased marginally up to 5-8% as compared to the equal ClO_2 doses at 25^0C. The observed results may be due to the combined effect of the initial rapid consumption of residual oxidant by the NOMs present in the source water samples and thermal decomposition of chlorate and chlorite ion.

Table 6. 3 Summary of ClO_2^- and ClO_3^- present in the source water and formed during Cl_2 and ClO_2 disinfection of seawater (SWR), river water (RVR), and reservoir water (RSR); Treatment conditions: Cl_2 and ClO_2 dose: 1, 3, 5, 10, and 25 mg/L, Contact time: 30 min-24 h; Temperature: 25^0C

		Conc. In source water (mg/L)		Treated water			
				ClO_2 treatment (1, 3, 5, 10, 25 mg/L)		Cl_2 treatment (1, 3, 5, 10, 25 mg/L)	
		ClO_2^-	ClO_3^-	ClO_2^-/ClO_2	ClO_3^-/ClO_2	ClO_2^-/Cl_2	ClO_3^-/Cl_2
Type of source water	SWR	nd	nd	0.15-0.31	0.00	NA	0.21-0.27
	RSR	nd	0.051	0.36-0.52	0.05-0.13	0.0-0.02	0.19-0.26
	RVR	nd	0.062	0.31-0.62	0.03-0.08	0.0	0.22-0.28
	DIW	NA	NA	0.15-0.39	0.0-0.12	0.0	0.31-0.37
4% NaOCl feed solution		nd	10200				

DIW: Deionized water (18mΩ), nd: not detected, NA: not available/not applicable; NaOCl feed solution was analyzed for chlorate and chlorite after 10,000 dilutions in deionized water. ClO_2^-/ClO_2, ClO_3^-/ClO_2, ClO_2^-/Cl_2, and ClO_3^-/Cl_2 represent the concentration of chlorite and chlorate formed per mg/L of ClO_2 and Cl_2 doses, respectively.

6.4 Conclusion

The formation trend and yield of THMs and HAAs during Cl_2 and ClO_2 treatments of water samples from three distinct natural sources, i.e., seawater, river water, and the open reservoir were systematically studied. This study demonstrated, the significant influence of source water type on DBPs formation. The net yield of TTHMs and HAAs due to increase in temperature was always observed to be positive for all the studied conditions. All studied water samples were susceptible for a significant amount of DBPs formation irrespective of the source. In general, the order of THMs formation potential of three water sources studied was RSR > SWR > RVR for chlorination whereas it was SWR > RSR > RVR for ClO_2 treatment. Total DBPs formed were always less for ClO_2 treatment as compared to that formed during chlorination irrespective of the water source type. HAAs were observed to be more readily formed than THMs during ClO_2 treatment, and the order was opposite for chlorination. Seawater demonstrated the highest bromine incorporation, thus leading to ~98% and 60-90% formation of brominated DBPs for both the oxidants. For river and reservoir water (fresh water), bromine incorporation percentage for THMs and HAAs were higher during ClO_2 treatment than Cl_2 treatment. High bromine incorporation may be a critical concern before shifting the water treatment from chlorine to chlorine dioxide as the brominated DBPs are known to be more toxic. However, our results of the three water sources indicated that health risk for ClO_2 treatment in terms of THMs and HAAs would be still lower than that for chlorination considering that the formation of both THMs and HAAs during ClO_2 treatment was both significantly lower. The propensity of bromine incorporation was observed to be more in THMs than in HAAs. For both Cl_2 and ClO_2 treatment, di-HAAs were dominant and more readily formed than Tri-HAAs followed by a small quantity of mono-HAAs regardless of the source water type. A significant amount of chlorate can be inadvertently introduced due to the contamination of the hypochlorite feedstock. ClO_2^- and ClO_3^- levels in the chlorine dioxide treated water varied between 15-31% and 0.0% for seawater, 36-52 % and 5-13% for reservoir water and 31-62% and 3-8% in river water respectively.

References

[1] S. Chowdhury, K. Alhooshani, T. Karanfil, Disinfection byproducts in swimming pool: Occurrences, implications and future needs, Water Res. 53 (2014) 68–109.

[2] T. Manasfi, M. De Méo, B. Coulomb, C. Di Giorgio, J.-L. Boudenne, Identification of disinfection by-products in freshwater and seawater swimming pools and evaluation of genotoxicity, Environ. Int. 88 (2016) 94–102.

[3] J. Wang, Z. Hao, F. Shi, Y. Yin, D. Cao, Z. Yao, J. Liu, Characterization of Brominated Disinfection Byproducts Formed during the Chlorination of Aquaculture Seawater, Environ. Sci. Technol. 52 (2018) 5662–5670.

[4] Z. Yang, Y.-X. Sun, T. Ye, N. Shi, F. Tang, H.-Y. Hu, Characterization of trihalomethane, haloacetic acid, and haloacetonitrile precursors in a seawater reverse osmosis system, Sci. Total Environ. 576 (2017) 391–397.

[5] USEPA, National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfection Byproducts Rule; Final rule, (2006) 399–493.

[6] J. Han, X. Zhang, Evaluating the Comparative Toxicity of DBP Mixtures from Different Disinfection Scenarios: A New Approach by Combining Freeze-Drying or Rotoevaporation with a Marine Polychaete Bioassay, Environ. Sci. Technol. 52 (2018) 10552–10561.

[7] X. Zhang, S. Echigo, R.A. Minear, M.J. Plewa, Characterization and Comparison of Disinfection By-Products of Four Major Disinfectants, in: S.E. Barrett, S.W. Krasner, G.L. Amy (Eds.), Nat. Org. Matter Disinfect. By-Products, American Chemical Society, Washington, DC, 2000: pp. 299–314.

[8] W. Gan, H. Huang, X. Yang, Z. Peng, G. Chen, Emerging investigators series: disinfection by-products in mixed chlorine dioxide and chlorine water treatment, Environ. Sci. Water Res. Technol. 2 (2016) 838–847.

[9] C. Korn, R.C. Andrews, M.D. Escobar, Development of chlorine dioxide-related by-product models for drinking water treatment, Water Res. 36 (2002) 330–342.

[10] X. Yang, W. Guo, W. Lee, Formation of disinfection byproducts upon chlorine dioxide preoxidation followed by chlorination or chloramination of natural organic matter, Chemosphere. 91 (2013) 1477–1485.

[11] H. Hong, Y. Xiong, M. Ruan, F. Liao, H. Lin, Y. Liang, Factors affecting THMs, HAAs and HNMs formation of Jin Lan Reservoir water exposed to chlorine and monochloramine, Sci. Total Environ. 444 (2013) 196–204.

[12] F. Al-Otoum, M.A. Al-Ghouti, T.A. Ahmed, M. Abu-Dieyeh, M. Ali, Disinfection by-products of chlorine dioxide (chlorite, chlorate, and trihalomethanes): Occurrence in drinking water in Qatar, Chemosphere. 164 (2016) 649–656.

[13] J. Han, X. Zhang, J. Liu, X. Zhu, T. Gong, Characterization of halogenated DBPs and identification of new DBPs trihalomethanols in chlorine dioxide treated drinking water with multiple extractions, J. Environ. Sci. 58 (2017) 83–92.

[14] S. Sorlini, F. Gialdini, M. Biasibetti, C. Collivignarelli, Influence of drinking water treatments on chlorine dioxide consumption and chlorite/chlorate formation, Water Res. 54 (2014) 44–52.

[15] G. Gordon, B. Slootmaekers, S. Tachiyashiki, W.W.I. Delmer, Minimizing Chlorite Ion and Chlorate Ion in Water Treated With Chlorine Dioxide, J. Am. Water Works Assoc. 82 (1990) 160–165.

[16] J. Deng, C. Liu, L. Yu, B. Zhou, Chronic exposure to environmental levels of tribromophenol impairs zebrafish reproduction, Toxicol. Appl. Pharmacol. 243 (2009) 87–95.

[17] J. Parinet, S. Tabaries, B. Coulomb, L. Vassalo, J.-L. Boudenne, Exposure levels to brominated compounds in seawater swimming pools treated with chlorine, Water Res. 46 (2012) 828–836.

[18] D.M. Golea, A. Upton, P. Jarvis, G. Moore, S. Sutherland, S.A. Parsons, S.J. Judd, THM and HAA formation from NOM in raw and treated surface waters, Water Res. 112 (2017) 226–235.

[19] C.-Y. Chang, Y.-H. Hsieh, S.-S. Hsu, P.-Y. Hu, K.-H. Wang, The formation of disinfection by-products in water treated with chlorine dioxide, J. Hazard. Mater. 79 (2000) 89–102.

[20] H.W. Yu, S.G. Oh, I.S. Kim, I. Pepper, S. Snyder, A. Jang, Formation and speciation of haloacetic acids in seawater desalination using chlorine dioxide as disinfectant, J. Ind. Eng. Chem. 26 (2015) 193–201.

[21] C.Y. Chang, Y.H. Hsieh, Y.M. Lin, P.Y. Hu, C.C. Liu, K.H. Wang, The organic precursors affecting the formation of disinfection by-products with chlorine dioxide, Chemosphere. 44 (2001) 1153–1158.

[22] D.R. Svenson, J.F. Kadla, H.-M. Chang, H. Jameel, Effect of pH on the Inorganic Species Involved in a Chlorine Dioxide Reaction System, Ind. Eng. Chem. Res. 41 (2002) 5927–5933.

[23] Y. Wang, H. Liu, Y. Xie, T. Ni, G. Liu, Oxidative removal of diclofenac by chlorine dioxide: Reaction kinetics and mechanism, Chem. Eng. J. 279 (2015) 409–415.

[24] B. Ramavandi, S. Farjadfard, M. Ardjmand, S. Dobaradaran, Effect of water quality and operational parameters on trihalomethanes formation potential in Dez River water, Iran, Water Resour. Ind. 11 (2015) 1–12.

[25] E.F. Xie, Disinfection byproducts in drinking water: formation, Analysis and control, Lewis Publisher, Washington DC, 2004.

[26] X. Yang, C. Shang, P. Westerhoff, Factors affecting formation of haloacetonitriles, haloketones, chloropicrin and cyanogen halides during chloramination, Water Res. 41 (2007) 1193–1200.

[27] R. Francois, Marine sedimentary humic substances-Structure, genesis and properties, Rev. Aquat. Sci. (1990) 41–80.

[28] C. Landry, L. Tremblay, Compositional Differences between Size Classes of Dissolved Organic Matter from Freshwater and Seawater Revealed by an HPLC-FTIR System, Environ. Sci. Technol. 46 (2012) 1700–1707.

[29] P.A. Maurice, M.J. Pullin, S.E. Cabaniss, Q. Zhou, K. Namjesnik-Dejanovic, G.R. Aiken, A comparison of surface water natural organic matter in raw filtered water samples, XAD, and reverse osmosis isolates, Water Res. 36 (2002) 2357–2371.

[30] S. Levesque, M.J. Rodriguez, J. Serodes, C. Beaulieu, F. Proulx, Effects of indoor drinking water handling on trihalomethanes and haloacetic acids, Water Res. 40 (2006) 2921–2930.

[31] H. Zhang, H. Dong, C. Adams, Z. Qiang, G. Luan, L. Wang, Formation and speciation of disinfection byproducts during chlor(am)ination of aquarium seawater, J. Environ. Sci. 33 (2015) 116–124.

[32] Y. Hong, H. Song, T. Karanfil, Formation of haloacetic acids from dissolved organic matter fractions during chloramination, (2013).

[33] K.K. Satpathy, Effect of biofouling on the cooling water quality of a nuclear power plant, Bull. Electrochem. (1999) 143–147.

[34] T. Nobukawa, S. Sanukida, Effect of bromide ions on genotoxicity of halogenated by-products from chlorination of humic acid in water., Water Res. 35 (2001) 4293–8.

[35] S. Regli, J. Chen, M. Messner, M.S. Elovitz, F.J. Letkiewicz, R.A. Pegram, T.J. Pepping, S.D. Richardson, J.M. Wright, Estimating Potential Increased Bladder Cancer Risk Due to Increased Bromide Concentrations in Sources of Disinfected Drinking Waters, Environ. Sci. Technol. 49 (2015) 13094–13102.

[36] E. Sawade, R. Fabris, A. Humpage, M. Drikas, Effect of increasing bromide concentration on toxicity in treated drinking water, J. Water Health. 14 (2016) 183–191.

[37] M.J. Plewa, J.E. Simmons, S.D. Richardson, E.D. Wagner, Mammalian cell cytotoxicity and genotoxicity of the haloacetic acids, a major class of drinking water disinfection by-products, Environ. Mol. Mutagen. 51 (2010) 871–878.

[38] H.H. Chang, H.H. Tung, C.C. Chao, G.S. Wang, Occurrence of haloacetic acids (HAAs) and trihalomethanes (THMs) in drinking water of Taiwan, Environ. Monit. Assess. 162 (2010) 237–250.

[39] J.A. Cotruvo, Nutrients in Drinking Water, World Health Organization, Geneva, 2005.

[40] J. Hu, H. Song, T. Karanfil, Comparative Analysis of Halonitromethane and Trihalomethane Formation and Speciation in Drinking Water: The Effects of Disinfectants, pH, Bromide, and Nitrite, Environ. Sci. Technol. 44 (2010) 794–799.

[41] H. Hong, X. Yan, X. Song, Y. Qin, H. Sun, H. Lin, J. Chen, Y. Liang, Bromine incorporation into five DBP classes upon chlorination of water with extremely low SUVA values, Sci. Total Environ. 590–591 (2017) 720–728.

[42] R.J. Garcia-Villanova, M.V. Oliveira Dantas Leite, J.M. Hernández Hierro, S. de Castro Alfageme, C. García Hernández, Occurrence of bromate, chlorite and chlorate in drinking waters disinfected with hypochlorite reagents. Tracing their origins, Sci. Total Environ. 408 (2010) 2616–2620.

[43] M. Bolyard, P.S. Fair, D.P. Hautman, Occurrence of chlorate in hypochlorite solutions used for drinking water disinfection, Environ. Sci. Technol. 26 (1992) 1663–1665.

[44] B.D. Stanford, A.N. Pisarenko, S.A. Snyder, G. Gordon, Perchlorate, bromate, and chlorate in hypochlorite solutions: Guidelines for utilities, J. Am. Water Work Assoc. 103 (2011) 1–13.

CHAPTER 7

THMs AND HAAs FORMATION POTENTIAL OF AQUAGENIC AND PEDOGENIC NATURAL ORGANIC MATTER SOURCE TO RAW WATER

Chapter 7

THMs and HAAs formation potential of aquagenic and pedogenic natural organic matter source to raw water

Abstract: This study investigated characteristics of algal organic matter (AOM) derived from *Spirulina Platensis*, bacterial derived organic matter from multispecies cultured bacterial suspension, and a composite soil sample from the surrounding landscape. Algal derived organic matter was divided as algal extracellular organic carbon (AEOC) and algal intracellular organic carbon (AIOC) and bacterial organic matter was separated as bacterial extracellular organic carbon (BEOC) and bacterial intracellular organic carbon (BIOC). Soil organic content (SOC) was extracted based on the conventional base (NaOH) and acid (HCl) leaching components as soil organic-base leachable (SOCB) and soil organic acid leachable (SOCA). The isolated algal, bacterial and soil organic content were further fractionated into hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) constituents based on the selective adsorption into XAD-4 and XAD-8 resin. All the organic fractions were treated with Cl_2 and ClO_2 to evaluate their specific THMs and HAAs potential. Speciation characteristics of THMs and HAAs during the Cl_2 and ClO_2 treatment of algal, bacterial and soil organic were also studied. The results indicated that algal EOC was the significant THMs contributor during chlorination, whereas, IOC and EOC contributed comparably for HAAs formation. Compared to chlorine, chlorine dioxide treatment resulted in significantly less THMs for both IOC and EOC, but HAAs formation during both the disinfectant treatments was similar. Formation of di-HAAs

predominates over tri-HAAs with the minuscule formation of mono halo HAAs during both chlorine and chlorine dioxide treatment of AOM. It was observed that, among SOCA and SOCB, SOCB fraction of the soil has lesser DBPs formation potential for both the disinfectants namely Cl_2 and ClO_2. Among all the soil constituents, only HPO and TPI of SOCA showed the formation of THMs during chlorine dioxide treatment with TPI (4.23 µg/mg-C) > HPO (1.03 µg/mg-C). Specific THMs formation potential (STHMFP) for chlorine treatment was the highest for HPO fraction of the SOCB and SOCA. For bacterial organic treatment, the vast variations in the DBPs formation behavior within the similar aqueous affinity (HPO, HPI, TPI) component made it difficult to identify a particular component as a major precursor type for THMs and HAAs formation during chlorination. The order of DBPs formation was TCM > DCAA > TCAA > BDCM > DBCM both for chlorine and chlorine dioxide treatment of bacterial organic. Compared to ClO_2 reaction with organic matter from algal and soil source, THMs: HAAs ratio was the highest for bacterial organic matter and may contribute in an appreciable amount to THM formation during ClO_2 treatment of natural water.

7.1 Introduction

Natural organic matter (NOM) in water bodies, a complex mixture of organic compounds, largely derived from terrestrial or aquatic primary producers and their biotic and abiotic transformations. Characteristic features of the NOMs is mostly associated with the source from which it is originally derived. Allochthonous input such as terrestrial NOMs derived from vegetation (pedogenic) and autochthonous from algae, bacteria and other organism degradation and metabolites (aquagenic) have distinct chemical features. For example, dissolved organic carbon (DOC) from aquatic algae is rich in nitrogen content and low in aromatic and phenolic carbon moiety. Whereas, NOM of terrestrial origin contains low nitrogen but high aromatic carbon and phenolic compounds. The distribution among each source is strongly dependent on climatological, hydrological and biogeochemical processes which also can alter the chemical structural and functional character of the NOM. For instance, NOM in freshwater is often enriched in lignin-derived polyphenols that originate from vascular plant debris [1,2]. The abundance of these polyphenols is typical for many rivers, lakes or wetlands. Marine DOM is comparably poor in these compounds [2,3]. It is widely recognized that phytoplankton is one of the main sources of organic matter in the sea and it contributes about 50 Gt/yr of organic carbon [4,5]. Similarly, heterotrophic bacteria are considered to be major contributors to the DOM pool in the ocean and even higher to coastal and freshwater environments [6]. Many studies demonstrated the ubiquitous nature of bacterially derived DOM in aquatic environments contributing to 20 to 40% of dissolved and particulate organic carbon [7,8]. It is indicated that bacterially derived organic matter could be a major source of organic matter in marine environments [6]. Terrestrial organic material inputs are mainly derived from the decomposition of plant debris, and the humification of organic matter originated from various land activities [9]. This allochthonous organic matter enters the aquatic systems mainly through subsequent runoff from overland water flow during rainfall events [10,11]. The relative contribution of the autochthonous and allochthonous processes to aquatic DOM varies among environments. The signature of DOM pool in the aquatic environments can be assumed as a blend of the end-member signatures of the input processes [10,12]. The terrestrial organic matter appeared to be the most significant near riverine–ocean interfaces, but measurable contributions have also been observed further offshore [13]. The relative influence of each end-member class determines the bulk chemical properties of the DOM, including hydrophobicity, drinking water treatment and biodegradation [14,15].

Presence of the natural organic matter (NOMs) is the basic cause for the formation of carbonaceous DBPs such as THMs and HAAs during water treatment [16,17]. Much attention has been paid to decipher the origin, transport, and fate of organic carbon in natural waters [3,18,19]. However, investigations to understand the origin of specific organic DBP precursor and their behavior are still lacking [20]. Amphiphilic character of complex aquatic natural organic matter, i.e., hydrophilic and hydrophobic component is one of the most important properties used for NOM classification with respect their reactivity with disinfectant for DBP formation [21–24]. NOM found in natural water is generally hydrophobic acids, which is reported to be made up approximately 50% of the DOC comprising of humic and fulvic acids [25]. The humic substances are generally regarded as the main cause of DBP formation [17]. For Instance, for one water source Krasner et al. (1996) [26] observed that hydrophobic fraction produced more than two times the concentration of THMs that formed with hydrophilic acid fraction. In contrast, observations reported by Croué et al. (1993) [27] and Owen et al. (1993) [28] showed that the hydrophilic fractions exerted the largest chlorine demand and greater THMs formation when compared to the hydrophobic material.

Several studies have reported a wide range of DBP yields upon the chlorination of NOMs, mainly focusing on allochthonous contribution to DBP formation, with negligible studies considering the contribution from phytoplankton and microbes [29] [30]. To the best of my knowledge, this is the first study from India that has addressed the DBP formation due to the various NOM sources to the aquatic system. Moreover, information on the role of chlorine dioxide on the formation of DBPs from the different NOMs sources is practically lacking. The present study is a comprehensive investigation of the disinfectant's reactivity with the various amphiphilic components of phytoplankton, bacteria, and soil derived organic matter. The main objectives of this study were (i) Characterisation of the NOMs derived from the extracellular and intracellular organic matter from phytoplankton and bacteria; acid and alkali leachable soil organic matter based on their hydrophobic, transphilic and hydrophilic constituents (ii) to investigate the reactivity of each fraction with chlorine and chlorine dioxide to determine the formation potential of two major class of carbonaceous DBPs such as THMs and HAAs.

7.2 Results and discussions

7.2.1 THMs and HAAs formation potential of algal-derived organic matter

7.2.1.1 Composition of algal organic matter

Algal derived organic matter (AOM) is generally dominated by organic nitrogen and carbon as compared to the aquatic NOM and prone to the formation of a significant amount of DBPs [31]**.** The level and nature of DBPs formation vary widely with algae species, algal growth stage, biochemical composition, and the disinfection conditions [31–35]. A complete understanding of the details of DBPs formation due to the intracellular and extracellular organic matter of different algae are very limited. Among the various algal species, cyanobacteria species are notorious for forming bloom. Because of their higher dissolved carbon and nitrogen contribution, they are of significant concern for the water utilities with regards to DBPs formation [29]. In this study, THMs and HAAs formation potential of the hydrophilic, hydrophobic and transphilic component of extracellular and intracellular organic carbon (EOC and IOC) of a cyanobacteria species, i.e. *Spirulina Platensis* was investigated. **Figure 7.1** shows the IOC and EOC contribution to the total algal organic carbon input by 10^6 cells of *Spirulina Platensis.* Intra-cellular organic carbon (IOC) content was observed to be 11 mg-C/10^6 algal cells harvested at the exponential phase whereas extracellular organic carbon content was 15.34 mg-C/10^6 cell. Thus, IOC accounted for 58%, and EOC contributed to 42% of total organic carbon input by *Spirulina Platensis* which is in agreement with the earlier report of lower yield of carbon content by extracellular algal organic [29]. In terms of distribution of different organic fractions; HPI, HPO, and TPI constituted 39%, 31% and 30% for IOC and 34%, 38% and 28% for EOC respectively (**Figure 7.1**). This observation is different from the finding of Li et al. (2012) [33] which was largely HPI dominated constituting about 60-90% of IOC and EOC in different algal species. Variability in algal species, growth conditions, nutrient availability and many other factors were known to alter the distribution of IOC and EOC production [36,37] and are likely to alter the biochemical composition.

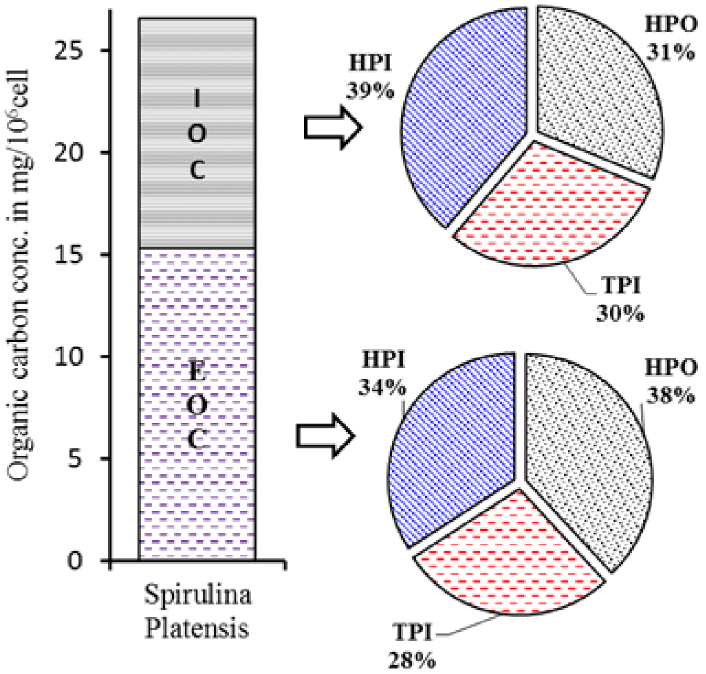


Figure 7. 1 The proportion of algal extracellular and intracellular organic carbon content (AEOC and AIOC) in *Spirulina Platensis* and their distribution into hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) constituents

7.2.1.2 THMs and HAAs yields

The reactivity of the total, HPI, TPI and HPI fractions of IOC and EOC towards chlorine and chlorine dioxide is presented in **Figure 7.2**. In general, it was observed that all the IOC and EOC fractions showed a higher degree of chlorine dioxide reactivity compared to chlorine. The large difference in the chlorine dioxide residual for 0.5 h and 24 h indicated the occurrence of incessant interactions with the organic matter, unlike chlorine where chlorine consumption was sluggish after the interaction with fast-reactive constituents of respective fractions except HPO and TPI of EOC. Though chlorine dioxide reactivity of the AOMs fractions was higher compared to chlorine, it did not reciprocately yield a higher amount of THMs or HAAs.

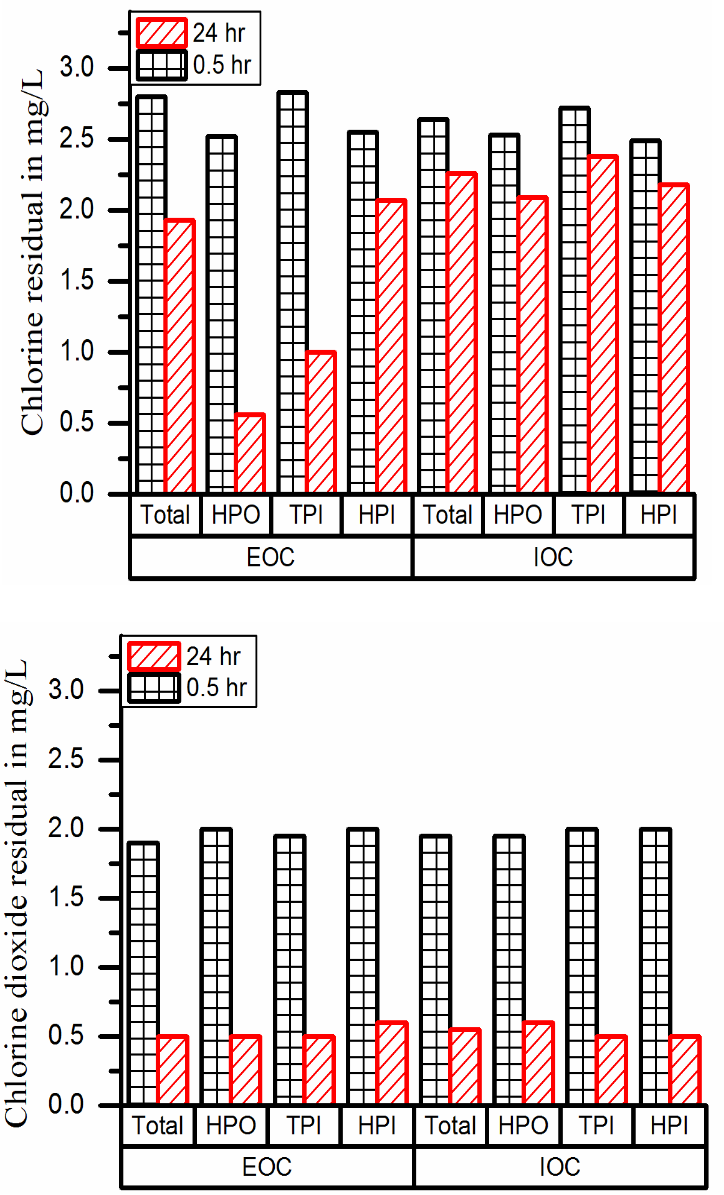


Figure 7. 2 Chlorine and chlorine dioxide residual remained after 0.5 h and 24 h of reaction time with algal (*Spirulina Platensis)* extracellular and intracellular organic matter (EOC- total and IOC-total) and their hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) constituents (Cl_2 and ClO_2 dose: 3 mg/L, carbon content adjusted to 1 mg/L)

In fact, both the THMs and HAAs yields during ClO_2 treatment was much less as compared to Cl_2 treatment. **Figure 7.2 (a), (b)** and **Figure 7.3 (a), (b)** illustrate the specific THMs and HAAs formation potential of HPI, HPO and TPI constituents of AOC and IOC during chlorine and chlorine dioxide treatment. The specific THMs formation potential (STHMFP) were 8.53, 16.3, and 16.94 µg/mg-C and 16.0, 5.62, and 3.36 µg/mg-C for HPO, TPI and HPI fractions of EOC and IOC respectively during chlorination (Cl_2 dose: 3 mg/L, reaction time: 24 h) (**Figure 7.2 (a)**). Whereas for chlorine dioxide treatment STHMFP were much lower compared to that for chlorine and observed to be 2.32, 2.02, and 1.65 µg/mg-C and 0.41, 0.93, and 0.0 µg/mg-C for HPO, TPI and HPI of EOC and IOC respectively (**Figure 7.2 (b)**). All the fractions of algal organic matter had shown the higher propensity of HAAs formation than THMs formation during both chlorination and chlorine dioxide treatment (**Figure 7.3 (a), (b)**). The specific HAAs formation potential (SHAAFP) were 19.54(5.73), 43.76(5.0), and 28.27(7.37) µg/mg-C and 48.51(10.81), 49.84(9.36), and 10.20(1.18) µg/mg-C for HPO, TPI and HPI fractions of EOC and IOC respectively during chlorine (chlorine dioxide) treatment (Cl_2/ClO_2 dose: 3 mg/L, reaction time: 24 h). Influenced by the relative distribution and preferential reactivity of HPI, HPO and TPI fractions, the formation potential of HAAs and THMs of the individual fractions were quite different compared to that for un-fractioned EOC and IOC in terms of the magnitude. In comparison to IOC contribution of 2.8 (1.21) µg/mg-C, EOC contributed 20.37 (2.61) µg/mg-C to the formation of THMs during chlorine (chlorine dioxide) treatment. Similarly, for HAAs, IOC and EOC contributed to 22.94 (25.48) µg/mg-C and 5.43 (4.82) µg/mg-C respectively for Cl_2 (ClO_2) treatment. It was indicated by the results that EOC was the significant THMs contributor during chlorination whereas IOC and EOC contributed comparably for HAAs formation. Compared to chlorine, chlorine dioxide treatment resulted in significantly less THMs for both IOC and EOC, but HAAs formation during both the disinfectant treatments was similar. Huang et al. (2009) [38], in their study, identified that specific yield of total THM and HAA from EOC were marginally higher as compared to IOC for one algal species whereas, the trend observed was opposite for a different strain by Li et al. (2012) [33]. It was generally inferred from the previous studies that species with a large surrounding mucilage component and high cellular exudation rate will have a greater contribution to the formation of DBPs [33,39]. In the present study, both HPO and TPI component of the AOC resulted in similar DBPs formation with comparable but lesser contribution from HPI fraction. The trend was similar for chlorine and chlorine dioxide with Cl_2 having 5 to 10 time more than ClO_2. In general, HPI is composed of carbohydrates, hydroxy acids, low molecular weight carboxylic acids, amino acids, amino sugars, peptides, low molecular weight alkyl alcohols, aldehydes, and ketones; while HPO comprises of hydrocarbons, high molecular weight alkylamines, fatty acids and aromatic acids, phenols and humic substances [40]. Thus, compared to algal HPI and TPI constituents, HPO fraction might represent as the better DBPs precursors.

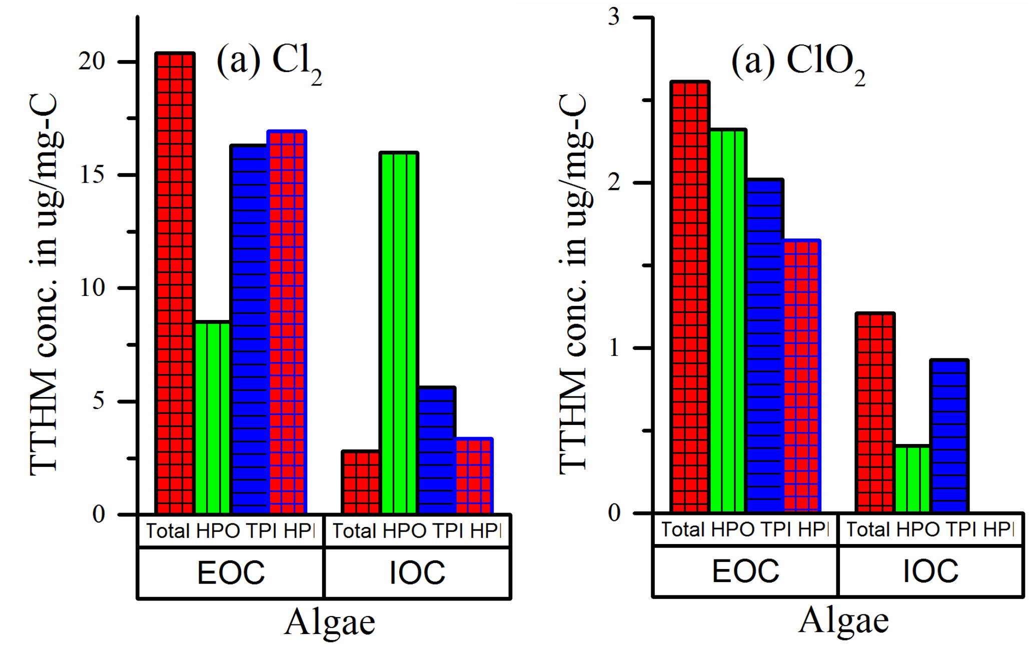


Figure 7. 3 TTHM formation potential of hydrophobic (HPO), transphilic (TPI) and hydrophilic content of algal (Spirulina Platensis) extracellular and intracellular organic carbon content (EOC and IOC) during (a) chlorine and (b) chlorine dioxide treatment (Cl_2; ClO_2: 3 mg/L, reaction time: 24 h)

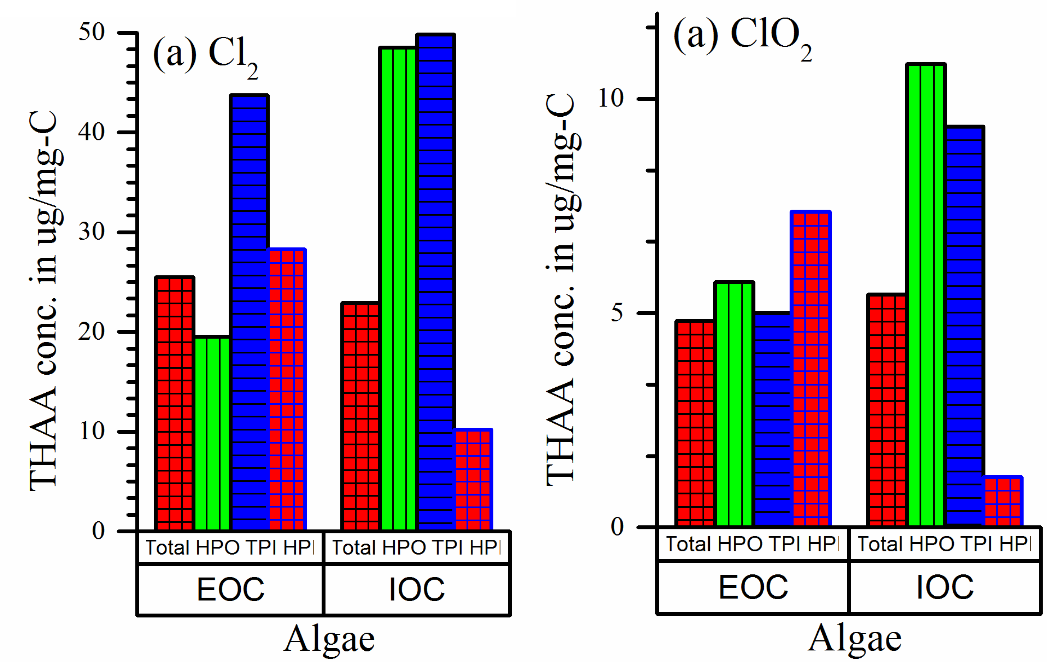


Figure 7. 4 THAA formation potential of hydrophobic (HPO), transphilic (TPI) and hydrophilic content of algal (*Spirulina Platensis*) extracellular and intracellular organic carbon content (AEOC and AIOC) during (a) chlorine and (b) chlorine dioxide treatment (Cl_2; ClO_2: 3 mg/L, reaction time: 24 h)

7.2.1.3 Effect of disinfectant doses

Figure 7.5 and **Figure 7.6** shows THMs and HAAs formation due to the treatment of EOC and IOC of *Spirulina Platensis* with different chlorine and chlorine dioxide doses. Both THMs and HAAs for EOC and IOC monotonically increased with increasing chlorine dose. EOC showed higher reactivity compared to IOC.

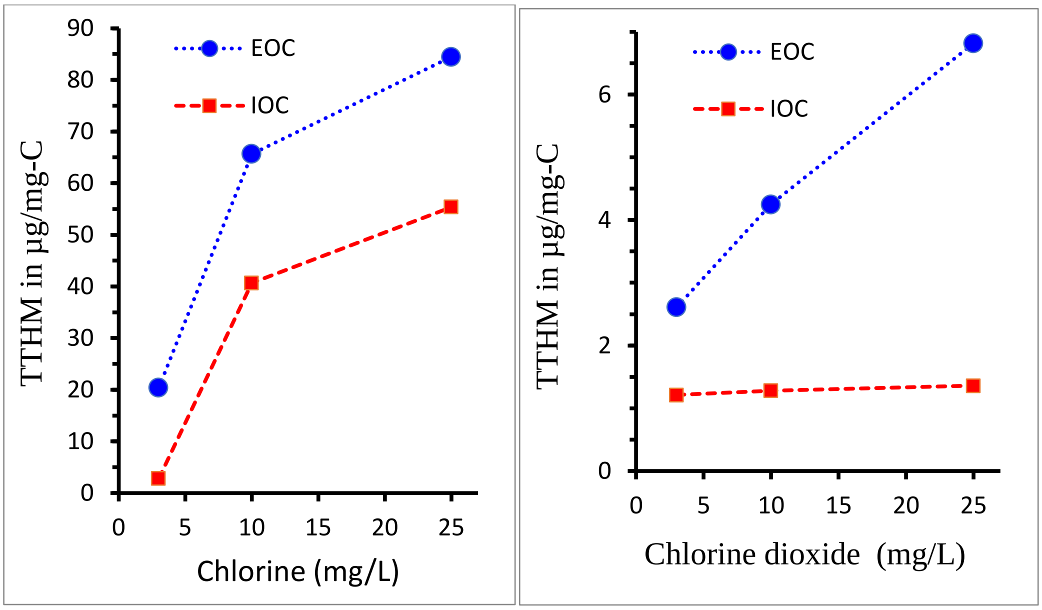


Figure 7. 5 Effect of chlorine dose on the specific THM formation potential of extracellular and intracellular organic content of Spirulina Platensis during chlorine and chlorine dioxide treatment (reaction time 24 h).

THM and HAA are assumed to be the final product of chlorination and thus stable in the presence of chlorine residual [41]. Therefore, the yield of THMs and HAAs generally increased with an increase in reaction time and chlorine dose till their precursor was exhausted. As expected, though the overall yield increased, the rate of formation decreased as the chlorine dose increased. The effect of chlorine dioxide dose on DBP formation demonstrated an unusual behavior. The total yield of THMs in treated IOC and HAAs in treated EOC remained almost unchanged as the ClO_2 dosed increased from 3 mg/L to 25 mg/L indicating the precursor limiting situation in the respective case. Though total THMs in the treated EOC increased as the ClO_2 dose increased, the decrease of HAAs on increasing the dose from 10- to 25 mg/L might be the result of decomposition or further oxidative breakdown of unstable HAAs initially formed.

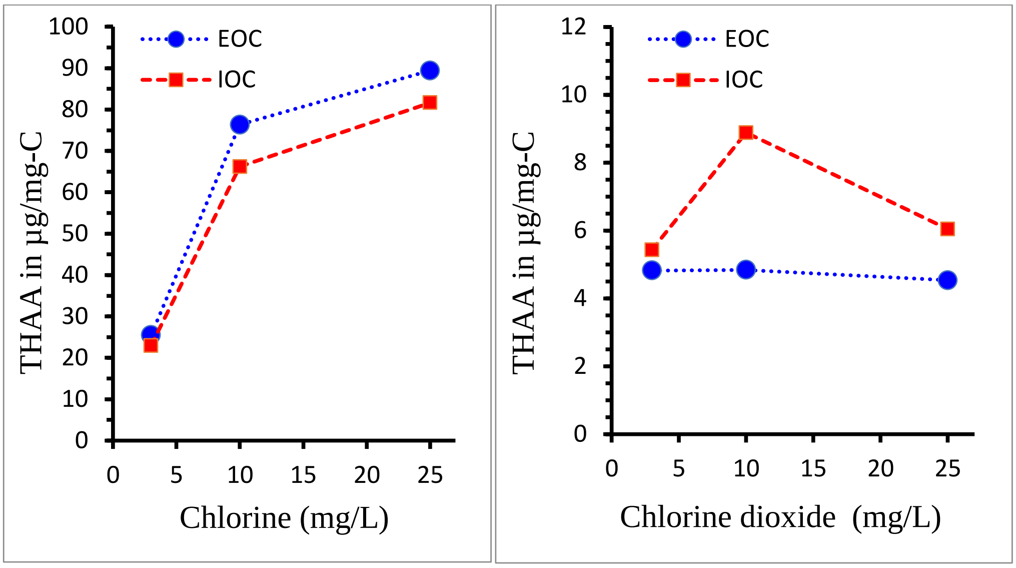


Figure 7. 6 Effect of chlorine dose on the specific HAA formation potential of extracellular and intracellular organic content of Spirulina Platensis during chlorine and chlorine dioxide treatment (reaction time 24 h)**.**

7.2.1.3 Distribution of HAAs and THMs species

Distribution of four THMs species and nine HAAAs species during chlorine and chlorine dioxide treatment of organic matter derived from *Spirulina Platensis* is presented in **Figure 7.7**. In terms of THMs speciation, the overall distribution order was BDCM > TCM > DBCM> TBM during chlorination. Impact of precursor characteristic was not found to be prominent to shift towards any particular THMs species. The lesser amount of TBM formed could be attributed to the oxidation of limiting amount of dissolved bromide present in the algal organic solution. However, compared to THMs, the characteristics of precursor had shown more impact on the

HAAs distribution. DCAA (46.3 %) and TCAA (45.5%) were clearly the dominating species accounting for almost 90% of the total HAAs formed per mg-C of algal organic matter. During ClO_2 treatment, THMs speciation order was TBM > TCM > BDCM > DBCM with much

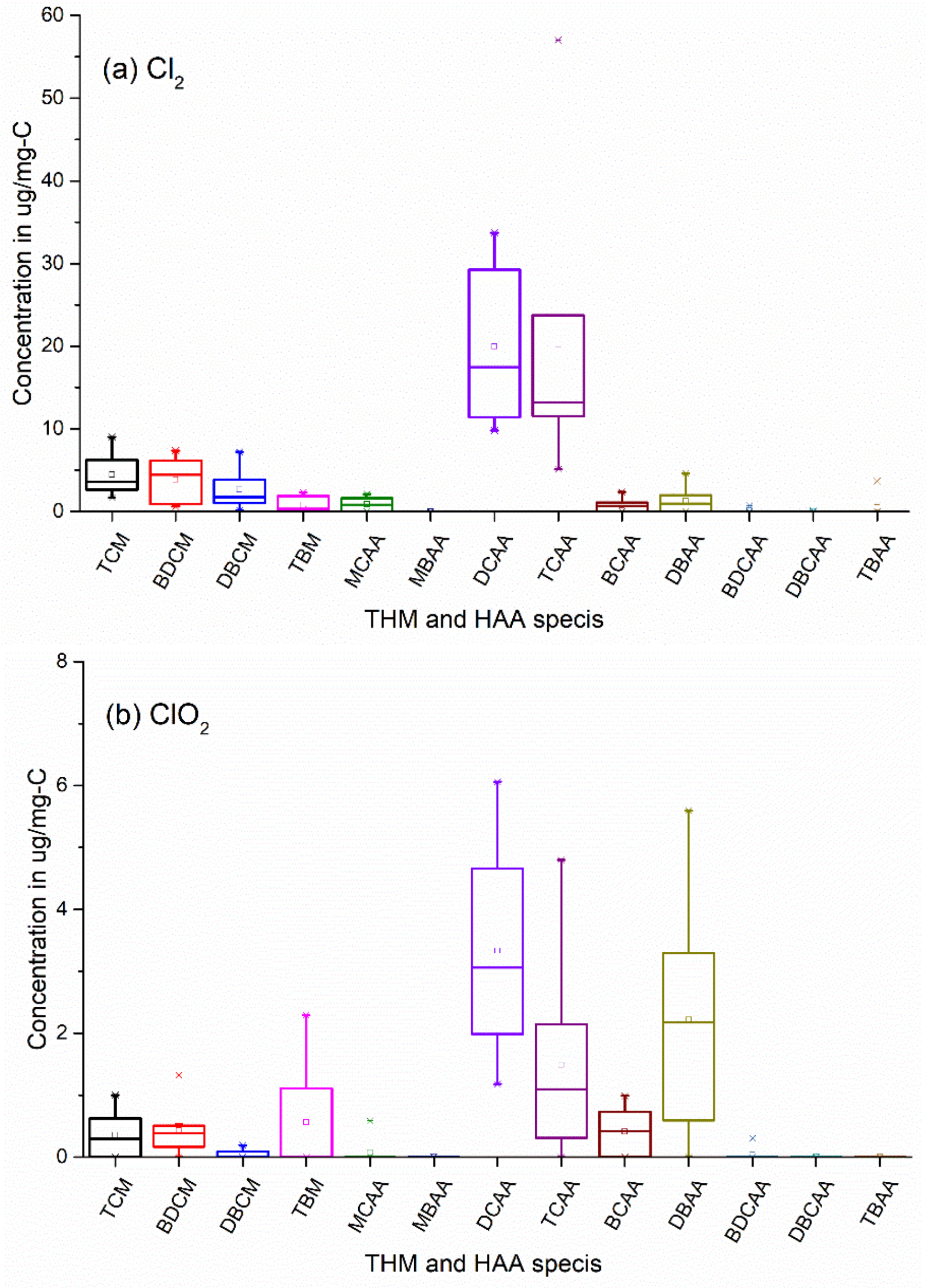


Figure 7. 7 Distribution of DBPs species (four THMs and nine HAAs) during chlorine and chlorine dioxide treatment of algal organic matter at various conditions.

lower concentration than that observed for chlorination. Bromine incorporation to be more profound during ClO_2 treatment than Cl_2 treatment. A significant percentage of DBAA and BCAA were formed during chlorine dioxide treatment which was much lesser during chlorine treatment. Four HAAs species; DCAA, DBAA, TCAA, and BCAA dominated the total HAAs contributing 44.13, 29.34, 19.68 and 5.43% respectively. Formation of di-HAAs predominates over tri-HAAs with the minuscule formation of mono halo HAAs during both chlorine and chlorine dioxide treatment of AOM. A previous investigation on the HAAs toxicity has proved that DCAA is a more potent carcinogen than TCAA [42]. A very high percentage of DCAA might be a concern when the treated water contains a high density of *Spirulina Platensis*. The dominance of di-HAA and tri-HAA was also observed by Huang et al. (2009) [38] during chlorination of two blue-green-algae species, and the overall finding was consistent with the observation that blue-green-algae may be a significant DBP precursor [43].

7.2.2 THMs and HAAs formation potential of soil-derived organic matter

7.2.2.1 Composition of soil organic matter

Though the NOM input from the degradation residue of aquatic organisms is important in eutrophic aquatic ecosystems, terrestrial input from the surrounding landscape is the primary NOMs source to inland water bodies [44]. Soil derived organic matter, primarily comprised of humic substances originated from vascular plants, is transported to streams, lakes, and estuaries in the form of dissolved organic carbon (DOC). This soil-derived organic matter input influences the physical, chemical, and biological features of recipient aquatic ecosystems significantly. In the present study, soil samples were collected from different places of the surrounding landscape and pooled together to prepare a homogeneous composite sample. The composite soil sample was extracted by the traditional acid (HCl) and alkali (NaOH) leaching. The isolated soil organic carbon, acid leachable (SOCA) and base leachable (SOCB) were further fractionated to their HPO, TPI and HPI components. Each fraction was subjected to chlorine and chlorine dioxide treatment experiments as mentioned earlier. **Figure 7.8** shows the composition of acid and base leachable soil organic carbon content (SOCA and SOCB) and their distribution into hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) constituents. The organic carbon content of the soil sample was 1.3% by weight. Base (alkali: 0.1 N NaOH) leachable organic content (SOCB) was 8.2 mg-C/g constituting 63.3% of the organic carbon content of the soil sample. Acid (0.1 N HCl) leachable organic content (SOCA) content of the remained soil residue was observed to be 4.8 mg-C/g and accounted for the 36.7 % of the total soil organic carbon. The distribution of HPO, TPI and HPI fractions in SOCB and SOCA were not identical indicating the presence of distinct organic moiety in the two categories of soil leachate. SOCA was dominated by HPI fraction constituting 46% whereas the same percentage of HPO organic carbon was observed in SOCB. In terms of distribution of TPI constituents, both SOCA and SOCB had a similar proportion of 24% and 25% respectively. These values are comparable to the respective DOC fractions for the surface water reported by Golea et al. (2017) and Zularisam et al. (2007) [21,45]. Variability in hydrological conditions, abiotic and biotic degradation, pH, the moisture content of the soil, aeration and many other factors were known cause transformation in the soil organic hydrophobicity [46,47].

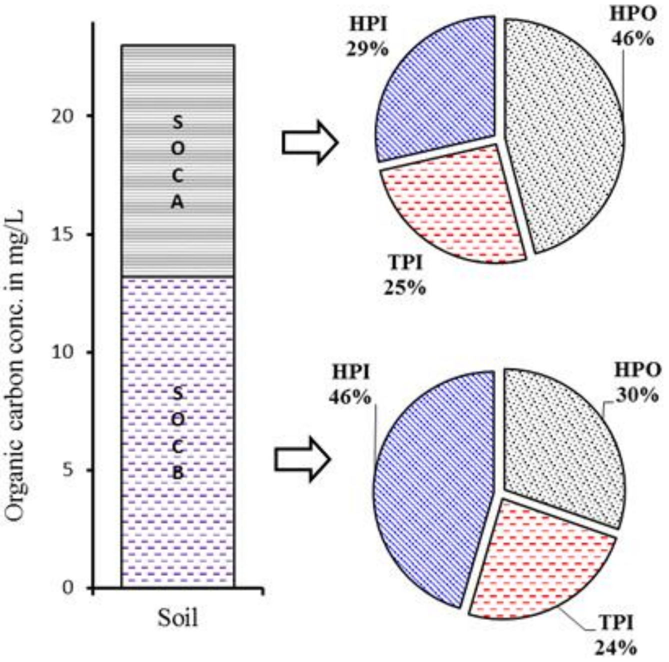


Figure 7. 8 The proportion of acid and base leachable soil organic carbon content (SOCA and SOCB) and their distribution into hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) constituents

7.2.2.2 THMs and HAAs yields

Polysaccharides, cellulose, and hemicellulose are biodegradable and labile soil organic matter fractions. Reactivity of these compounds towards chlorine is less and thus they generally do not produce large amounts of DBPs [48]. In contrast, the humic substances, lignin residues, and plant-based phenolics are far less biodegradable and may accumulate over the short term [49]. These structures are quite reactive with chlorine due to their active functional groups and high electron density in the aromatic rings. As a result, they can produce higher amounts of DBPs upon chlorine or other disinfectant treatment. All the soil organic component, namely SOCA-total, SOCB total, and their HPO, TPI and HPI fractions were adjusted to 1 mg/L of organic carbon content and treated with Cl_2 and a ClO_2 dose of 3 mg/L. Residual disinfectant available at the end of 0.5 h and 24 h reaction time was evaluated. **Figure 7.9** presents the chlorine consumption character of the soil fractions. It was observed for both Cl_2 and ClO_2 treatment that the HPI fraction, particularly the SOCA-HPI fraction was most reactive in terms of total disinfectant consumption and kinetics. Chlorine demand of the SOCA-total and SOCB-total was similar. SOCB-total exhibited higher ClO_2 demand compared to SOCA-total though the trend of individual fractions was the opposite.

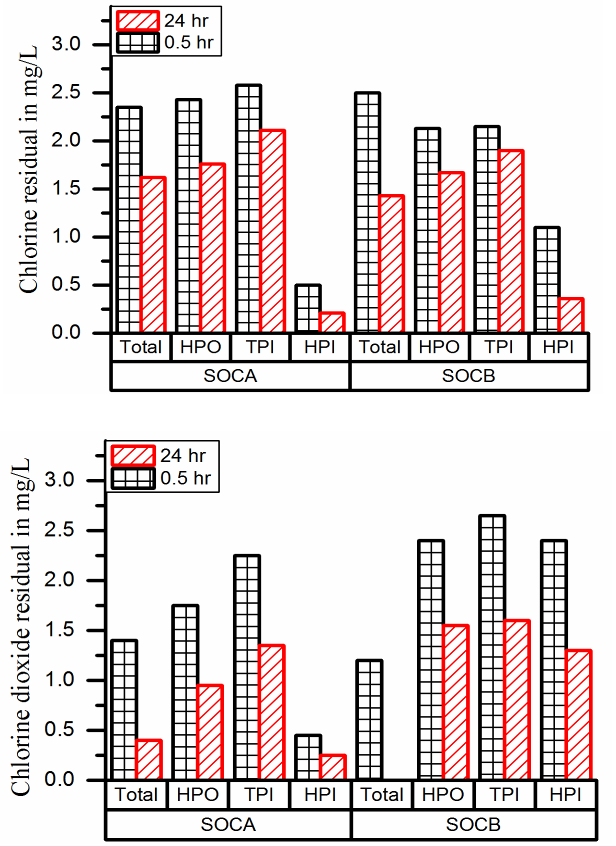


Figure 7. 9 Chlorine and chlorine dioxide residual remained after 0.5 h and 24 h of reaction time with acid and base leachable soil organic matter (SOCA- total and SOCB-total) and their hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) constituents (Cl_2 and ClO_2 dose: 3 mg/L, carbon content adjusted to 1 mg/L)

In general, 3 mg/L of Cl_2 and ClO_2 was sufficient to display residual even after 24 h of contact time. Specific THM formation potential (STHMFP) and specific HAA formation potential (SHAAFP) of the soil organic carbon is presented in **Figure 7.10** and **Figure 7.11** respectively. It was observed that the SOCB fraction of the soil has the lesser DBPs formation potential for both the disinfectants. Among all the soil constituents, only HPO and TPI of SOCA showed formation THMs during chlorine dioxide treatment with TPI (4.23 µg/mg-C) > HPO (1.03 µg/mg-C). THMs concentration of SOCA-total and SOCB-total remained undetectable during ClO_2. In contrast, the reactivity of both acid and base soluble soil organic carbon towards chlorine was very high compared to chlorine dioxide. STHMFPs of SOCA and SOCB were 251.2 µg/mg-C and 191.3 µg/mg-C. The order of STHMFPs for chlorine treatment was HPO > HPI > TPI for SOCA and HPO > TPI > HPI for SOCB with comparably lower value (**Figure 7.10**). In a similar study for soil samples from Twitchell Island and Webb Tract in the central Delta, it was reported that THMFP of HPO fraction was significantly higher than all other fractions [50]. Our results for SOCB soil organic were similar to the order of relative reactivity among fractions found in other studies: HPO> TPI > HPI [28,51,52]. This indicates the diverse nature of organic carbon present in the constituents of the soil. Unlike the insignificant formation of THMs during ClO_2 treatment, both the SOCA and SOCB of the soil showed significant reactivity for HAAs formation (**Figure 7.11**) though it was still much lower as compared to the values observed for the chlorine treatment. SOCA-TPI and SOCB-HPO showed highest SHAAFPs for both Cl_2 and ClO_2 treatment. The SHAAFPs of soil constituents were SOCA: - total: 67.2 (11.1), HPO:86.36(12.22), TPI: 192.4(28.37), HPI: 142.55(23.40) µg/mg-C and SOCB: - total: 114.9(11.86), HPO:195.96(16.16), TPI: 103.2 (10.38), HPI: 149.86(24.10) µg/mg-C for 24 h reaction with 3 mg/L of Cl_2 (ClO_2) (**Figure 7.11**). As indicated in the results, THMs and HAAs formation of the soil derived organic matter was much higher in case of chlorine treatment than that of chlorine dioxide treatment.

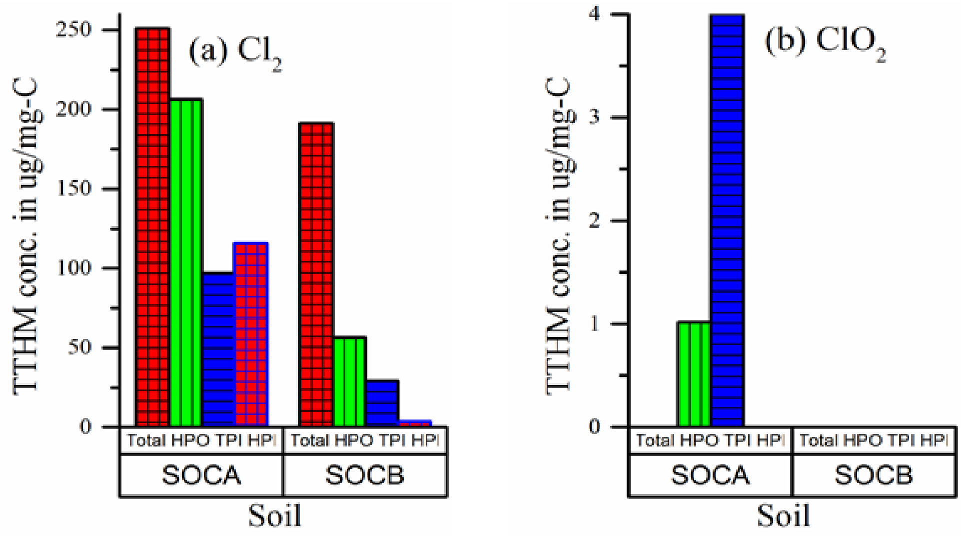


Figure 7. 10 TTHM formation potential of hydrophobic (HPO), transphilic (TPI) and hydrophilic content of acid and base leachable soil organic carbon content (SOCA and SOCB) during (a) chlorine and (b) chlorine dioxide treatment (Cl_2; ClO_2: 3 mg/L, reaction time: 24 h)

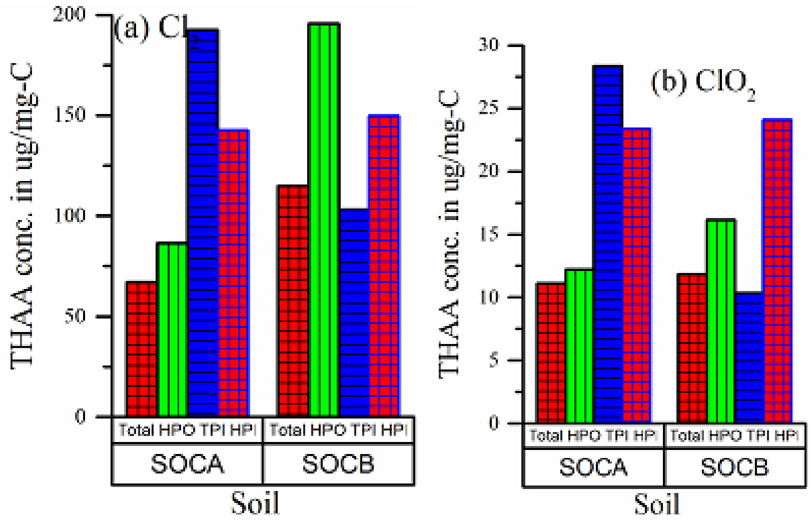


Figure 7. 11 THAA formation potential of hydrophobic (HPO), transphilic (TPI) and hydrophilic content of acid and base leachable soil organic carbon content (SOCA and SOCB) during (a) chlorine and (b) chlorine dioxide treatment (Cl_2; ClO_2: 3 mg/L, reaction time: 24 h)

7.2.2.3 Effect of disinfectant doses

The effect of Cl_2 and ClO_2 dose on the THMs and HAAs yield of SOCA-total and SOCB-total is presented in **Figure 7.12 and Figure 7.13**. THMs formation with respect to SOCA constituent of soil organic carbon showed higher slope as the disinfectant dose increased from 3 mg/L to 25 mg/L during Cl_2 and ClO_2 treatment. The yield of THMs and HAAs was increased to a significant extent with increasing the disinfectant dose, though the specific rate of formation (per mg/L of Cl_2 and ClO_2) became sluggish at higher disinfectant doses. The dose-response was lowest for the HAAs formation in SOCB during chlorine treatment, thus indicating the limited availability of chlorine reactive precursor in that constituents. In terms of percentage of yield, the dose-response for THMs and HAAs formation was always higher for ClO_2 treatment indicating that as the ClO_2 dose increased, more and more organic moiety took part in the reaction or the less reactive organic moiety transformed to became active precursor.

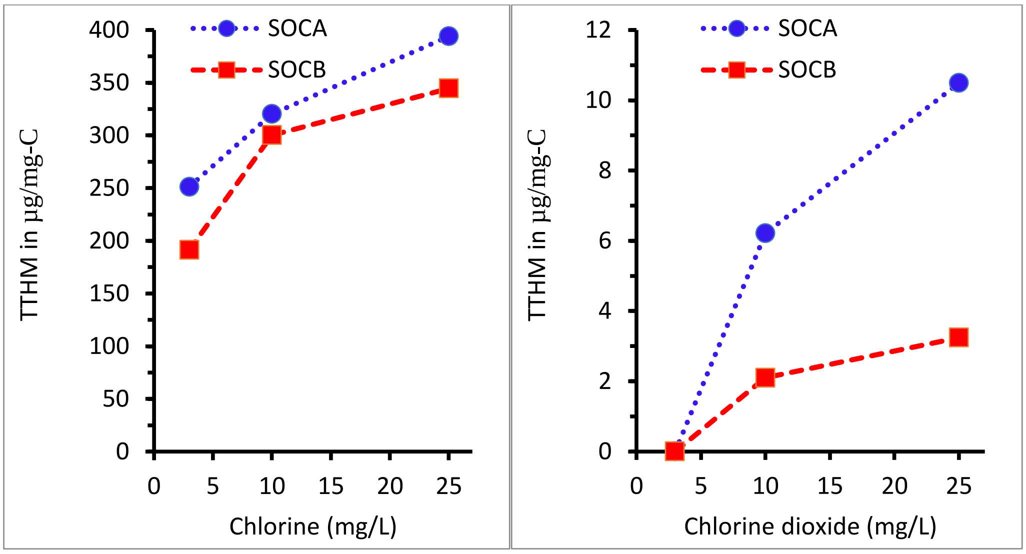


Figure 7. 12 Effect of chlorine dose on the specific THM formation potential of acid and base leachable organic content of soil during chlorine and chlorine dioxide treatment (reaction time 24 h)**.**

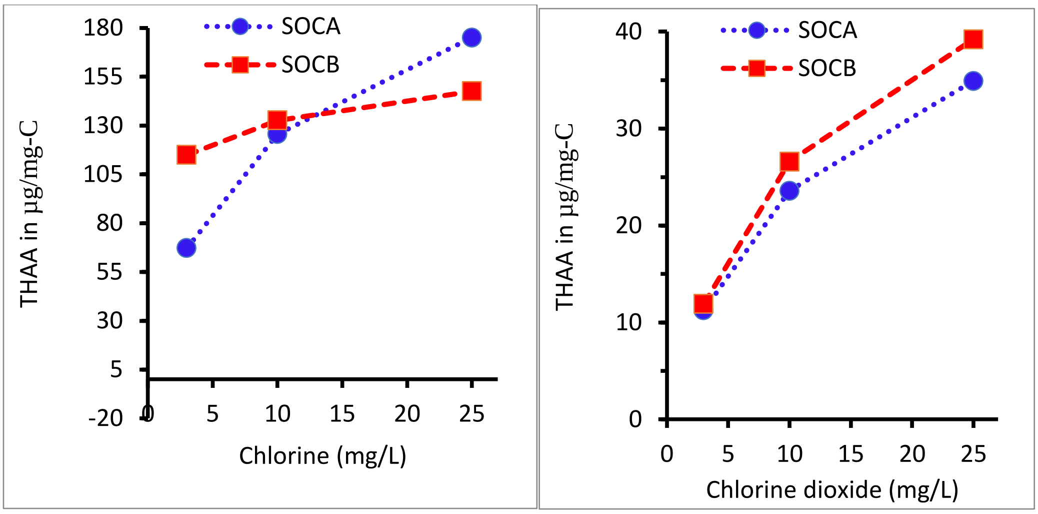


Figure 7. 13 Effect of chlorine dose on the specific HAA formation potential of acid and base leachable organic content of soil during Cl_2 and ClO_2 treatment (reaction time 24 h).

Whereas, in the case of chlorine the reaction progressed with a very high initial yield involving most of the easily reactive precursor and the reaction progressed with the slow reactive organic moiety further. The results showed that the precursor responsible for the THMs and HAAs might be different and the reactivity of the chlorine dioxide with the HAAs precursor is more prominent than that with THMs precursor. However, the reactivity pattern was opposite for chlorine and more and more THMs were formed than HAAs as the dose increased.

7.2.2.4 Distribution of HAAs and THMs species

The distribution pattern of THMs and HAAs were markedly different in case of chlorine and chlorine dioxide treatment with soil organic matter. **Figure 7.14** illustrates the species distribution of four THMs and nine HAAs species observed during the chlorine and chlorine treatment of various organic constituents of soil. During chlorination, THMs species distributed in the order TBM > DBCM > BDCM > TCM. The dominance of TBM indicates the presence of an appreciable amount of soluble bromide in the soil matrix as the soil sample. It was also possible that the organic matter is composed of the brominated functional group which subsequently resulted in more brominated THMs. BDCM was the frequently detected THMs species during ClO_2 treatment. The speciation characteristic of HAAs during Cl_2 and ClO_2 were entirely different. TBAA and mono-HAAs were the lowest formed HAAs; other HAAs species were significantly formed during chlorination. The order of distribution was DCAA > DBAA > BDCAA > TCAA > DBCAA > BCAA (**Figure 7.14 (a)**). The HAAs distribution character is quite different to that observed for chlorination of algal organic matter showing the significant impact of precursor properties and nature of disinfectant on the HAAs species distribution. During ClO_2 treatment, DBAA formation varied more widely among the different constituents of soil organic matter, with the average value highest among other HAAs species. The order of average values of HAAs formation for ClO_2 treatment was DBAA > DCAA > TCAA > BCAA. TCAA was the only tri-HAAs species formed during chlorine dioxide treatment in contrast to chlorine where the tri-HAA formed were TCAA, BDCAA, and DBCAA. Since the overall THMs formation was low, its speciation behavior is of less importance during ClO_2 treatment.

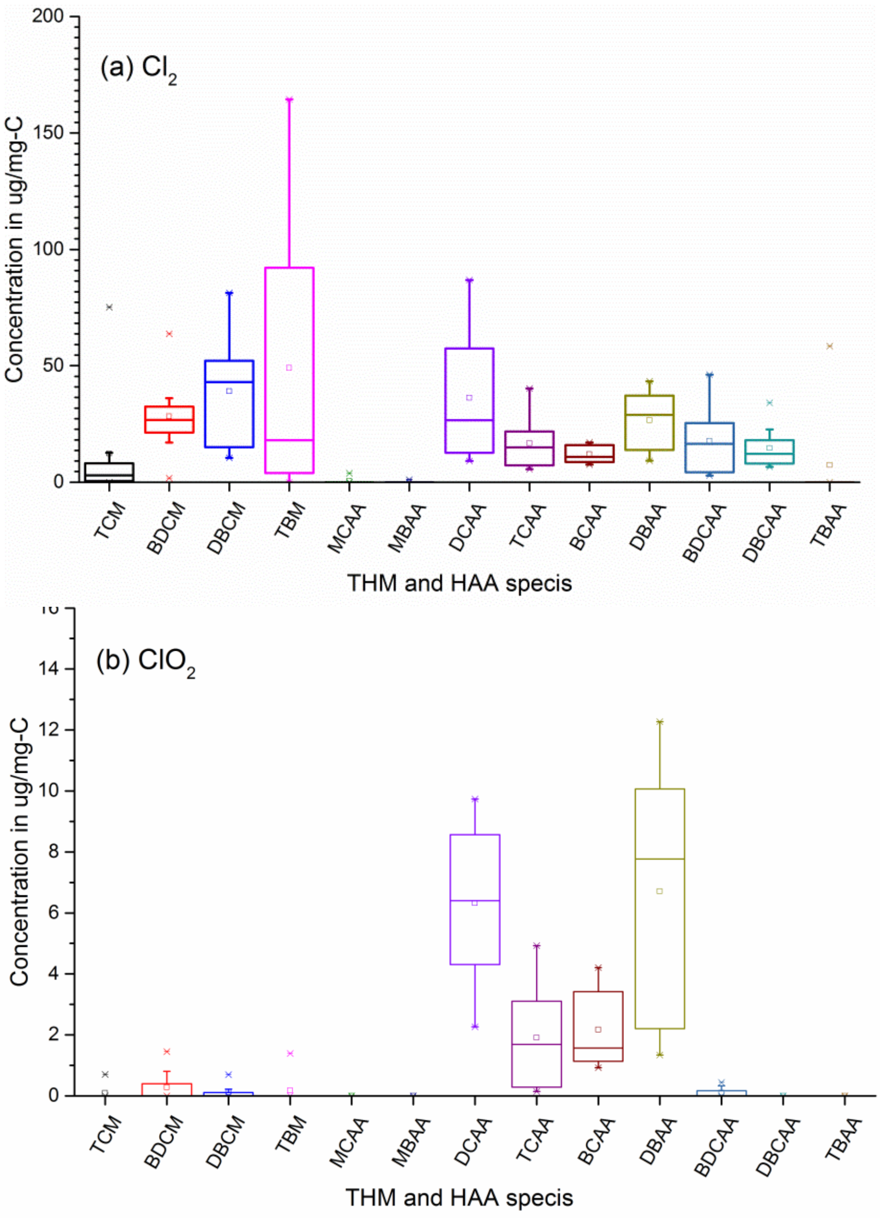


Figure 7. 14 Distribution of DBPs species (four THMs and nine HAAs) during chlorine and chlorine dioxide treatment of soil organic matter at various conditions

7.2.3 THMs and HAAs formation potential of bacterial organic matter

Biofilm formation is a universal phenomenon in water utility network, high concentrations of organic matter may accumulate on biofilm surfaces which can be a potential source of THMs and HAAs precursor [53,54]. As discussed in the previous section, algal-derived organic matter can generate a wide range of DBPs. Algal extracellular organic matter possesses similar chemical composition as biofilm extracellular polymeric substances (EPS) and reactivity to disinfectant [41,55]. Thus, biofilm may contribute significantly to the DBPs formation in the water network. DBP formation due to the interaction of disinfectants with biofilm is currently not well studied [56], and as such, no study is available which compares its reactivity and DBPs formation with different disinfectants such as Cl_2 and ClO_2. Recent studies on DBPs formation from bacterial cell have demonstrated that bacterial-derived organic carbon facilitated DBP formation upon chlorination [55]. In the present study, the influence of extracellular and intracellular biomolecules and different constituents fractionated based on their water affinity on DBP formation, and speciation was investigated. THMs and HAAs formation experiments were conducted with two disinfectants namely Cl_2 and ClO_2.

7.2.3.1 Composition of bacterial organic matter

Biofilm samples were scraped from experimental titanium panels which were immersed in coastal water for 48 h. The biofilm containing bacteria was cultured in Zobell marine broth for 72 h to obtain amplified dense bacterial suspension. Extracellular and intracellular organic components were separated and fractionated into HPO, TPI and HPI constituents as per the procedure described in the materials and methodology chapter. **Figure 7.15** represents the distribution of various components of the bacterial-derived organic matter. Extracellular and intracellular organic carbon (BEOC and BIOC) content of the mixed bacterial suspension was 108.2 and 270.1 mg/L which was estimated to be 10.8 and 27.0 fg-C $cell^{-1}$ respectively. The bacterial carbon content observed was in agreement with the average carbon content of 12.4 and 30.2 fg C cell^{-1} for heterotrophic bacteria present in offshore and coastal seawater respectively [8]. Aqueous extract of BEOC and BIOC was appropriately diluted and fractionated into HPO, TPI and HPI components. BIOC was TPI dominated with 53% followed by HPI (27%) and HPO (20%), whereas, EOC which contributed less than half of IOC was dominated by HPI (46%) followed by TPI (28%) and HPO (26%). The aqueous affinity character of the organic fractions was observed to be significantly different from that typically observed for surface water dissolved organic matter wherein HPI represents 50-70% of total DOC [57].

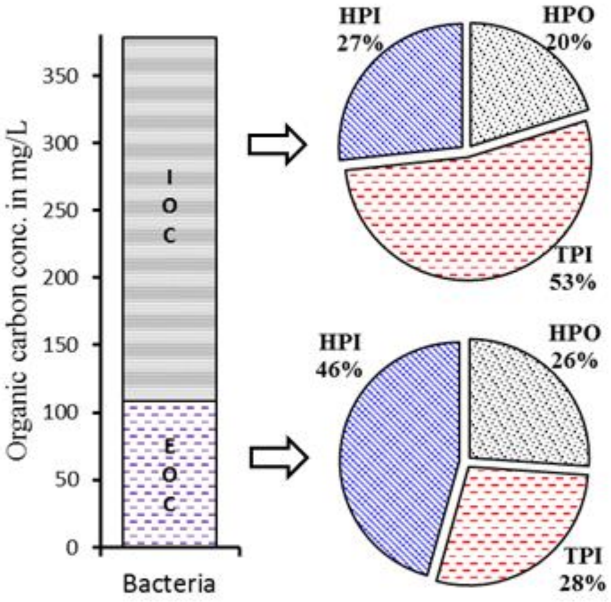


Figure 7. 15 The proportion of IOC and EOC of bacterial organic carbon content (BIOC and BEOC) and their distribution into hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) constituents

Variation in typical composition were often reported, for example, Yu et al. (2015) [59] reported that seawater used for their study to be consisted of 30% HPO, 57% and 13% TPI. In another instance, the organic matter present in the influent of potable water treatment plant was reported to consists of 60% HPI and 40% HPO [60]. Since the aquatic DOM is a mixture of dissolved organic material derived from different autochthonous and allochthonous source, its amphiphilic character would be expected to be different from that of bacterial-derived DOC. Further, the structural characteristic of biomolecules produced by bacteria varies according to the environment and bacteria species as well.

7.2.3.2 THMs and HAAs yields

Considering the reports from other studies, bacterial EOC and IOC need to be considered as a significant precursor to DBP formation [30,56]. The compositions and structures of biomolecules can affect DBP formation and speciation. The isolated bacterial EOC, IOC and their HPO, TPI and HPI fractions were adjusted to 1 mg-C/L and treated with 3 mg/L of chlorine and chlorine dioxide. Residual Cl_2 and ClO_2 available after 0.5 h and 24 h were determined and presented in **Figure 7.16**. Among the unfractionated bacterial organic content, BIOC exhibited higher chlorine reactivity than BEOC. Though the reactivity trend of BIOC and BEOC with ClO_2 was similar to Cl_2, the variations in the available residual were lesser in case of chlorine dioxide as compared to chlorine. In general, ClO_2 showed rapid initial decay followed by a relatively sluggish decay profile. The decay kinetics of ClO_2 was observed to be not affected greatly with the difference in precursor properties possibly present in different fractions of BIOC and BIOC. Whereas, substantial variations in the respective available residual values for both 0.5 h and 24 h during the Cl_2 treatment of HPO, TPI and HPI fractions of bacterial organic content indicated the primary involvement of functionally different organic biomolecules which might not be common to different fractions.

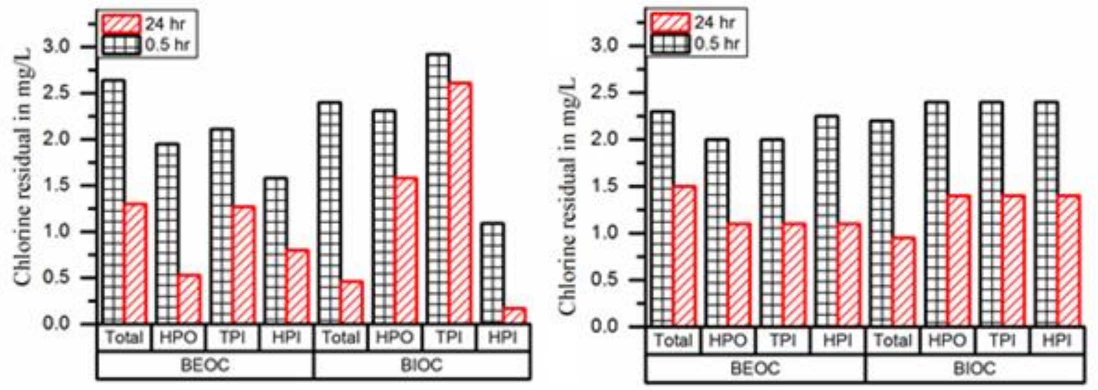


Figure 7. 16 Chlorine and chlorine dioxide residual remained after 0.5 h and 24 h of reaction time with IOC and EOC of bacterial organic carbon (BIOC- total and BEOC-total) and their hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) constituents (Cl_2 and ClO_2 dose: 3 mg/L, carbon content adjusted to 1 mg/L)

Among all the constituents, TPI fraction of BIOC showed the least reactivity to chlorine (**Figure 7.16**) and the same was reflected as the lowest values of STHMFPs and SHAAFPs observed for chlorine treatment of TPI-BIOC (**Figure 7.17 and Figure 7.18**). In contrast, the TPI of BEOC showed the highest THMs formation and second highest HAAs formation during chlorination. This difference in the DBPs formation character indicated the structural difference of the same transphilic organic component of extracellular and intracellular bacterial organic biomolecules. Similarly, BIOC-HPI showed highest chlorine reactivity, however, the reaction did not lead to reciprocate formation of THMs and HAAs (**Figure 7.17 and Figure 7.18**). Overall, the order of STHMFPs for chlorination was; BEOC: TPI > HPI > HPO, BIOC: HPO > HPI > TPI and the order of SHAAFPs was BEOC: HPI > TPI > HPO, BIOC: HPI > HPO > TPI.

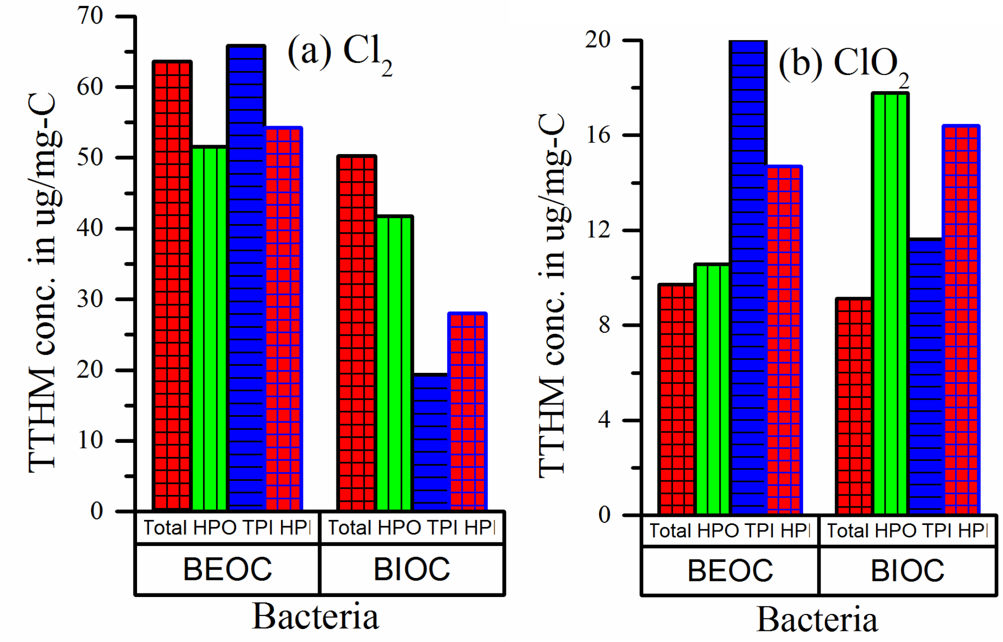


Figure 7. 17 TTHM formation potential of hydrophobic (HPO), transphilic (TPI) and hydrophilic content of IOC and EOC of bacterial organic carbon content (BIOC and EIOC) during (a) chlorine and (b) chlorine dioxide treatment (Cl_2; ClO_2: 3 mg/L, reaction time: 24 h)

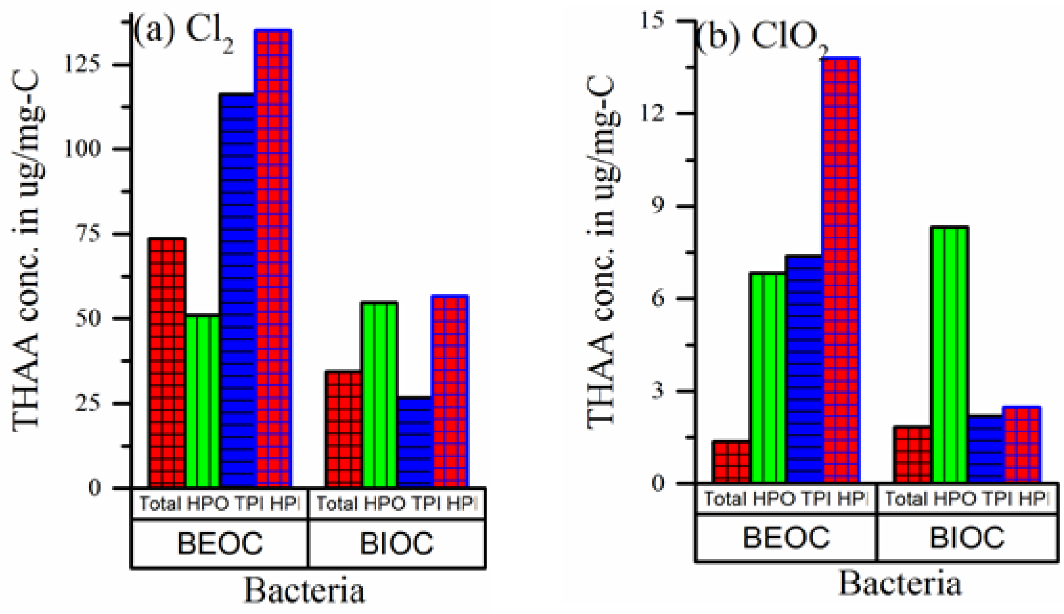


Figure 7. 18 THAA formation potential of hydrophobic (HPO), transphilic (TPI) and hydrophilic content of IOC and EOC of bacterial organic carbon content (BIOC and EIOC) during (a) chlorine and (b) chlorine dioxide treatment (Cl_2; ClO_2: 3 mg/L, reaction time: 24 h)

The vast variations in the DBPs formation behavior of organic components with a similar aqueous affinity (HPO, HPI, TPI) made it difficult to identify a particular component as a major precursor type for THMs and HAAs formation during chlorination. One important observation was that bacterial organic matter was susceptible to the formation of a significant amount of THMs compared to algal and soil organic matter (**Figure 7.17**). STHMFPs values ranged from 10.58 µg/mg-C of BEOC-HPO (lowest) to 20.15 µg/mg-C BEOC-HPI (highest). SHAAFPs of bacterial organic matter was within the range that observed for chlorine dioxide treatment of soil and algal organic matter. Thus, a higher ratio of THMs to HAAs during chlorine dioxide treatment of raw water may be an indicator of the dominance of bacterial organic matter input to the aquatic system. The result indicated that fractions of BEOC were the major contributor for HAAs formation during ClO_2 treatment with its HPI fraction showed the highest value. However, a higher yield of THMs and HAAs for the individual fractions compared to the total IOC and EOC as in the case of HAAs and THMs formation during ClO_2 treatment of BEOC occurred in many cases of algal and soil organic matter could not be explained with the present information on the structural contribution and disinfectant reactivity.

7.2.3.3 Effect of disinfectant doses

It was repeatedly demonstrated that formation of DBPs increases monotonously due to the transformation and additional participation of less reactive NOMs fraction as the disinfectant dose increased during water treatment [23,61–63]. The effect of disinfectant dose on the formation of THMs and HAAs was described in **Figure 7.19** and **Figure 7.20**. The bacterial organic matter also responded positively to the increased disinfectant dose with a higher yield of THMs and HAAs.

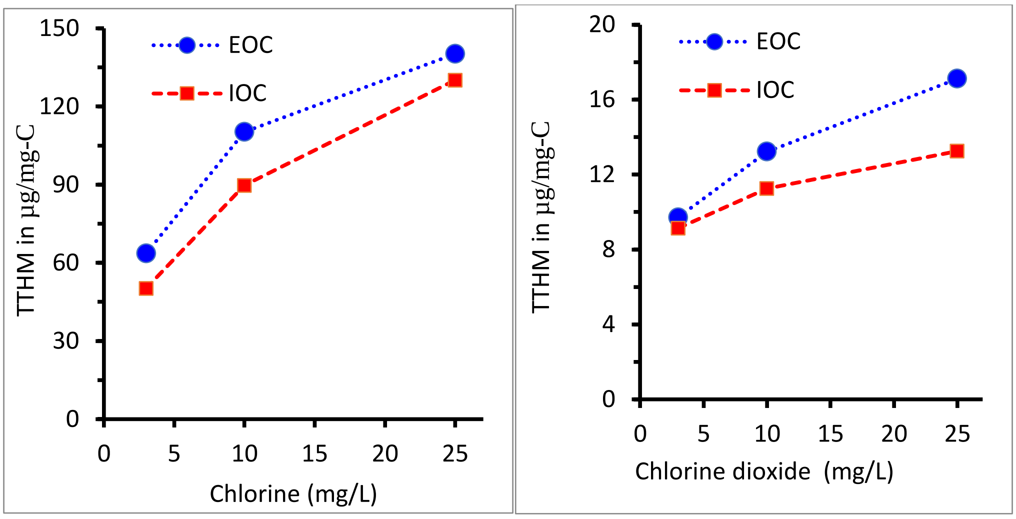


Figure 7. 19 Effect of dose on the specific THM formation potential of IOC and EOC of bacterial organic carbon during chlorine and chlorine dioxide treatment (reaction time 24 h).

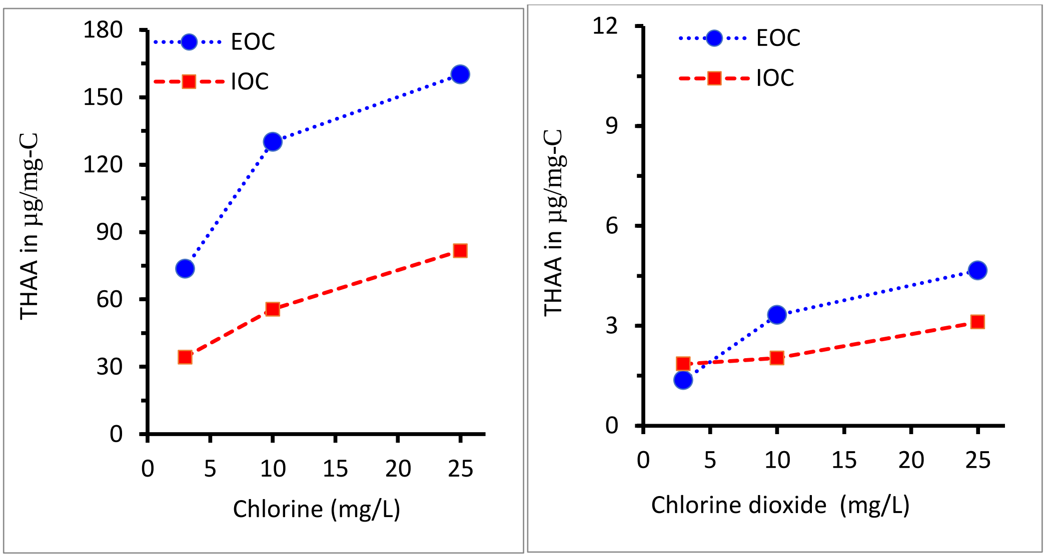


Figure 7. 20 Effect of dose on the specific HAA formation potential of IOC and EOC of bacteria during chlorine and chlorine dioxide treatment (reaction time 24 h).

For chlorination, BIOC and BEOC responded positively to the increased dose almost similarly which was of course associated with the lower initial concentration of THMs for BIOC. THMs formed after 24 h of 3 mg/L of Cl_2 treatment was 63.6 and 50.2 µg/L for BEOC and BIOC respectively which increased to 140.2 and 130.11 µg/L for

25 mg/L Cl_2, thus registering a 2-3 time increase with more than 8 time increase in dose. Similar was the trend for HAAs, its concentration after 24 h of reaction time increased from 73.7 and 34.3 μg/L to 160.1 and 81.65 μg/L for BEOC and BIOC respectively for an increase of Cl_2 dose from 3 to 25 mg/L (**Figure 7.19**). The response of THMs and HAAs formation to increase in chlorine dioxide dose was more sluggish compared to that for chlorine (**Figure 7.20**). This may be due to the active participation of ClO_2 radical in DOC elimination by oxidation over the chlorine substitution of DOC. The other possibility was that at higher ClO_2 concertation, the chance of interaction with active sites such as -OH and -OCH_3 becomes more predominant to produce other reaction products and the formation of halogenated DBPs such as THMs and HAAs was inhibited [64].

7.2.3.4 Distribution of HAAs and THMs species

The present study compares the species distribution of nine HAAs and four THMs during the Cl_2 and ClO_2 treatment of bacterial-derived biomolecule. It is previously reported that the chemical composition of bacterial organic matter played a significant role in DBP yield and speciation [55]. **Figure 7.21** shows the detailed speciation of THMs and HAAs formed separately during chlorine and chlorine dioxide treatment. Chloroform was the highest among all DBPs. BDCM was the second highest THMs species formed at a concentration much lower than chloroform. The THMs speciation trend was similar for Cl_2 and ClO_2 treatment. In terms of HAAs species, DCAA yield was the highest followed by TCAA for both the disinfectant treatment. Compared to algal and soil organic matter DBPs speciation, where HAAs species were more distributed, bacterial organic matter resulted in the HAAs speciation to be dominantly

DCAA and TCAA which could be attributed to the biomacromolecule rich in DCAA precursor [65].

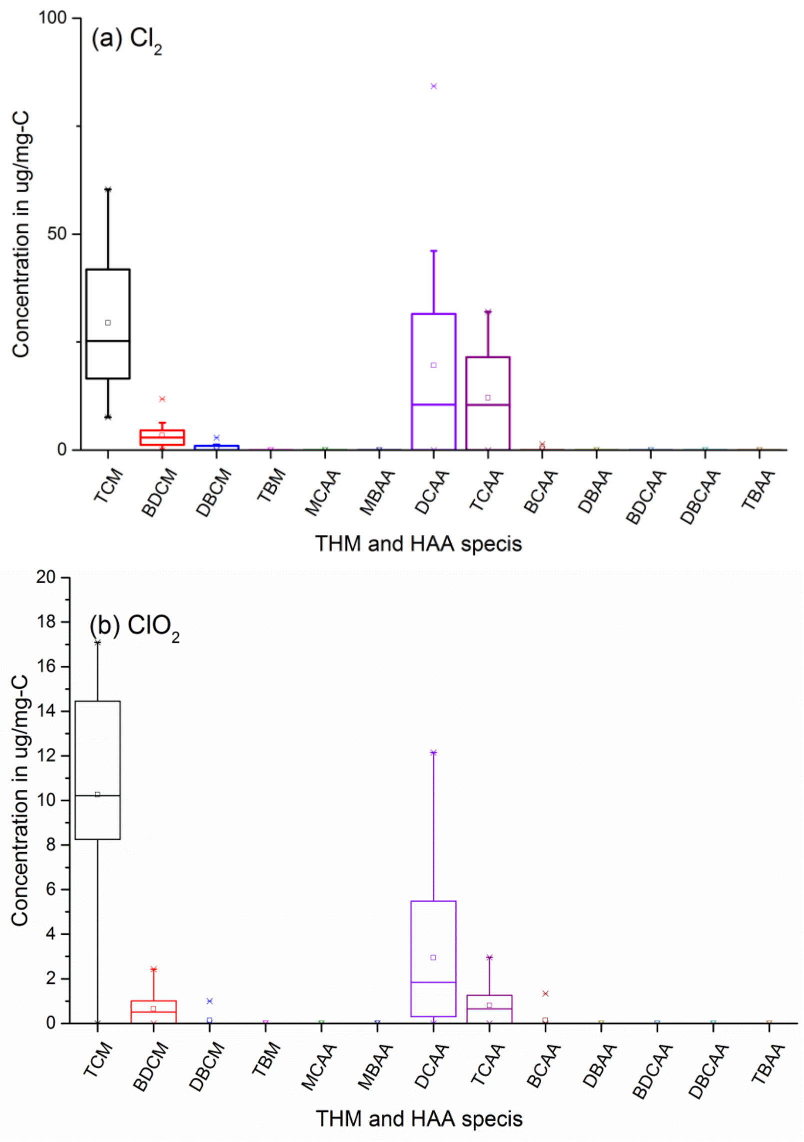


Figure 7. 21 Distribution of DBPs species (four THMs and nine HAAs) during chlorine and chlorine dioxide treatment of bacterial organic matter at various conditions

The order of DBPs formation was TCM > DCAA > TCAA > BDCM > DBCM both for chlorine and chlorine dioxide treatment. The average value of DCAA to TCAA ratio was 2.24:1 for chlorine and 6.3:1 for chlorine dioxide treatment. This indicated that the precursor involved for TCAA formation was less reactive to ClO_2 than chlorine. From this study it was revealed that the change in the disinfectant from chlorine to chlorine dioxide did not affect the THMs and HAAs species trend, however, the yield in case of ClO_2 was much lower. Compared to ClO_2 reaction with organic matter from algal and soil source THMs: HAAs ratio was the highest for bacterial organic matter and may contribute an appreciable amount of THM in ClO_2 treated natural water.

7.3 Conclusion

Algal, bacterial and soil organic content was characterized and their contribution to DBP formation was evaluated. Influenced by the relative distribution and preferential reactivity of HPI, HPO and TPI fractions of EOC and IOC, the formation potential of HAAs and THMs of the individual fractions were quite different compared to that with un-fractioned algal and bacterial EOC and IOC in terms of the magnitude. Higher yield of THMs and HAAs for the individual fractions compared to the total IOC and EOC as in the case of HAAs and THMs formation during ClO_2 treatment of BEOC. Algal EOC was associated with higher THMs and IOC was associated with higher HAAs formation indicating different precursor composition of IOC and EOC. Formation of di-HAAs predominated over tri-HAAs during both chlorine and chlorine dioxide treatment of AOM. Among the algal, bacterial and soil organic matter, STHMFPs and SHAAFPs of soil demonstrated the highest value. SOCA-TPI and SOCB-HPO showed the highest SHAAFPs for both Cl_2 and ClO_2 treatment. The results showed that the precursor responsible for the formation of THMs may be different to HAAs precursor, and the reactivity of the chlorine dioxide with the HAAs precursor is more prominent than that with THMs precursor for soil organic carbon.

Since the overall THMs formation was low for the soil organics, its speciation behavior is of less importance during ClO_2 treatment. For bacterial derived organic matter, overall, the order of STHMFPs for chlorination was; BEOC: TPI > HPI > HPO, BIOC: HPO > HPI > TPI and the order of SHAAFPs was BEOC: HPI > TPI > HPO, BIOC: HPI > HPO > TPI. The order of DBPs formation was TCM > DCAA > TCAA > BDCM > DBCM both for chlorine and chlorine dioxide treatment. The average value of DCAA to TCAA ratio was 2.24:1 for chlorine and 6.3:1 for chlorine dioxide treatment. This indicated that the precursor involved for TCAA formation was less reactive to ClO_2 than chlorine. One more important observation was that ClO_2 treatment of bacterial organic matter generates an appreciable amount of THMs which was least formed in the case of algal and soil organic matter and may contribute to THM load in ClO_2 treated natural water. Though organic matter derived from all the sources such as algal, bacterial and soil organic has significant potential for the CBPs formation, soil-derived organic matter showed the highest formation potential and to be considered as a part of DBP control plan. Since algal organic matter showed high consumption of ClO_2 than Cl_2, application of chlorine dioxide to natural water containing high algal content or during the event such as algal bloom has to be checked carefully for the availability of the desired residual.

References

[1] M.A. Goñi, J.I. Hedges, Lignin dimers: Structures, distribution, and potential geochemical applications, Geochim. Cosmochim. Acta. 56 (1992) 4025–4043.

[2] K.J. Meyers-Schulte, J.I. Hedges, Molecular evidence for a terrestrial component of organic matter dissolved in ocean water, Nature. 321 (1986) 61–63.

[3] S. Opsahl, R. Benner, Distribution and cycling of terrigenous dissolved organic matter in the ocean, Nature. 386 (1997) 480–482.

[4] B. Biddanda, R. Benner, Carbon, nitrogen, and carbohydrate fluxes during the production of particulate and dissolved organic matter by marine phytoplankton, Limnol. Oceanogr. 42 (1997) 506–518.

[5] U. Siegenthaler, J.L. Sarmiento, Atmospheric carbon dioxide and the ocean, Nature. 365 (1993) 119–125.

[6] N. Kawasaki, K. Komatsu, A. Kohzu, N. Tomioka, R. Shinohara, T. Satou, F.N. Watanabe, Y. Tada, K. Hamasaki, M.R.M. Kushairi, A. Imai, Bacterial contribution to dissolved organic matter in eutrophic Lake Kasumigaura, Japan., Appl. Environ. Microbiol. 79 (2013) 7160–8.

[7] K. Kaiser, R. Benner, Major bacterial contribution to the ocean reservoir of detrital organic carbon and nitrogen, Limnol. Oceanogr. 53 (2008) 99–112.

[8] N. Kawasaki, R. Sohrin, H. Ogawa, T. Nagata, R. Benner, Bacterial carbon content and the living and detrital bacterial contributions to suspended particulate organic carbon in the North Pacific Ocean, Aquat. Microb. Ecol. 62 (2011) 165–176.

[9] H. Mash, P.K. Westerhoff, L.A. Baker, R.A. Nieman, M.-L. Nguyen, Dissolved organic matter in Arizona reservoirs: assessment of carbonaceous sources, Org. Geochem. 35 (2004) 831–843.

[10] D.M. McKnight, E.W. Boyer, P.K. Westerhoff, P.T. Doran, T. Kulbe, D.T. Andersen, Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity, Limnol. Oceanogr. 46 (2001) 38–48.

[11] G.D. Onstad, D.E. Canfield, P.D. Quay, J.I. Hedges, Sources of particulate organic matter in rivers from the continental USA: Lignin phenol and stable carbon isotope compositions, 2000.

[12] G.E. Tenzer, P.A. Meyers, J.A. Robbins, B.J. Eadie, N.R. Morehead, M.B. Lansing, Sedimentary organic matter record of recent environmental changes in the St. Marys River ecosystem, Michigan–Ontario border, Org. Geochem. 30 (1999) 133–146.

[13] S. Mitra, T.S. Bianchi, L. Guo, P.H. Santschi, Terrestrially derived dissolved organic matter in the chesapeake bay and the middle atlantic bight, Geochim. Cosmochim. Acta. 64 (2000) 3547–3557.

[14] R. L. Malcolm, The uniqueness of humic substances in each of soil, stream and marine environments, Anal. Chim. Acta. 232 (1990) 19–30.

[15] P. Westerhoff, G. Aiken, G. Amy, J. Debroux, Relationships between the structure of natural organic matter and its reactivity towards molecular ozone and hydroxyl radicals, Water Res. 33 (1999) 2265–2276.

[16] M. Kitis, T. Karanfil, J.E. Kilduff, A. Wigton, The reactivity of natural organic matter to disinfection by-products formation and its relation to specific ultraviolet absorbance., Water Sci. Technol. 43 (2001) 9–16.

[17] S.A. Parsons, B. Jefferson, E.H. Goslan, P.R. Jarvis, D.A. Fearing, Natural organic matter-the relationship between character and treatability, Water Sci. Technol. Water Supply. 4 (2004) 43–48.

[18] J.A. Aitkenhead, D. Hope, M.F. Billett, The relationship between dissolved organic carbon in stream water and soil organic carbon pools at different spatial scales, Hydrol. Process. 13 (1999) 1289–1302.

[19] D. Hope, M.F. Billett, M.S. Cresser, A review of the export of carbon in river water: Fluxes and processes, Environ. Pollut. 84 (1994) 301–324.

[20] D.A. Reckhow, P.L.S. Rees, D. Bryan, Watershed sources of disinfection byproduct precursors, Water Sci. Technol. Water Supply. 4 (2004) 61–69.

[21] D.M. Golea, A. Upton, P. Jarvis, G. Moore, S. Sutherland, S.A. Parsons, S.J. Judd, THM and HAA formation from NOM in raw and treated surface waters, Water Res. 112 (2017) 226–235.

[22] E.H. Goslan, Natural Organic Matter Character and Reactivity: Assessing Seasonal Variation in a Moorland Water, (2003).

[23] D. Gang, T.E. Clevenger, S.K. Banerji, Relationship of chlorine decay and THMs formation to NOM size, J. Hazard. Mater. 96 (2003) 1–12.

[24] W. Gan, W. Guo, J. Mo, Y. He, Y. Liu, W. Liu, Y. Liang, X. Yang, The occurrence of disinfection by-products in municipal drinking water in China’s Pearl River Delta and a multipathway cancer risk assessment, Sci. Total Environ. 447 (2013) 108–115.

[25] C. Jung, H. Son, The relationship between disinfection by-products formation and characteristics of natural organic matter in raw water, Korean J. Chem. Eng. 25 (2008) 714–720.

[26] S.W. Krasner, J.-P. Croué, J. Buffle, E.M. Perdue, Three approaches for characterizing NOM, J. Am. Water Works Assoc. 88 (1996) 66–79.

[27] J.P. Croué, E. Lefebvre, B. Martin, B. Legube, Removal of Dissolved Hydrophobic and Hydrophilic Organic Substances during Coagulation/Flocculation of Surface Waters, Water Sci. Technol. 27 (1993) 143–152.

[28] D.M. Owen, G.L. Amy, Z.K. Chowdhury, Character- ization of Natural Organic Matter and Its Relationship to Treatability, AWWA Research Foundation and American Water, Denver, CO, USA., 1993.

[29] A. Tomlinson, M. Drikas, J.D. Brookes, The role of phytoplankton as pre-cursors for disinfection by-product formation upon chlorination, Water Res. 102 (2016) 229–240.

[30] Z. Wang, O. Choi, Y. Seo, Relative contribution of biomolecules in bacterial extracellular polymeric substances to disinfection byproduct formation, Environ. Sci. Technol. 47 (2013) 9764–9773.

[31] T. Chen, Disinfection By-products Formation after Coagulation of Algal Extracellular and Intracellular Organic Matters, (2017).

[32] H. Lv, J. Yang, L. Liu, X. Yu, Z. Yu, P. Chiang, Temperature and nutrients are significant drivers of seasonal shift in phytoplankton community from a drinking water reservoir, subtropical China, Environ. Sci. Pollut. Res. 21 (2014) 5917–5928.

[33] L. Li, N. Gao, Y. Deng, J. Yao, K. Zhang, Characterization of intracellular & extracellular algae organic matters (AOM) of Microcystic aeruginosa and formation of AOM-associated disinfection byproducts and odor & taste compounds, Water Res. 46 (2012) 1233–1240.

[34] Y.S. Lui, J.W. Qiu, Y.L. Zhang, M.H. Wong, Y. Liang, Algal-derived organic matter as precursors of disinfection by-products and mutagens upon chlorination, Water Res. 45 (2011) 1454–1462.

[35] J. Huang, N. Graham, M.R. Templeton, Y. Zhang, C. Collins, M. Nieuwenhuijsen, A comparison of the role of two blue-green algae in THM and HAA formation, Water Res. 43 (2009) 3009–3018.

[36] T.H. Mague, E. Friberg, D.J. Hughes, I. Morris, Extracellular release of carbon by marine phytoplankton; a physiological approach1, Limnol. Oceanogr. 25 (1980) 262–279.

[37] C.S. Reynolds, The Ecology of Freshwater Phytoplankton, in: Cambridge University Press, 1984: p. 150.

[38] J. Huang, N. Graham, M.R. Templeton, Y. Zhang, C. Collins, M. Nieuwenhuijsen, A comparison of the role of two blue–green algae in THM and HAA formation, Water Res. 43 (2009) 3009–3018.

[39] M.-L. Nguyen, P. Westerhoff, L. Baker, Q. Hu, M. Esparza-Soto, M. Sommerfeld, Characteristics and Reactivity of Algae-Produced Dissolved Organic Carbon, J. Environ. Eng. 131 (2005) 1574–1582.

[40] J.K. Edzwald, Coagulation in Drinking Water Treatment: Particles, Organics and Coagulants, Water Sci. Technol. 27 (1993) 21–35.

[41] J. Fang, J. Ma, X. Yang, C. Shang, Formation of carbonaceous and nitrogenous disinfection by-products from the chlorination of Microcystis aeruginosa, Water Res. 44 (2010) 1934–1940.

[42] R.J. Bull, Mode of action of liver tumor induction by trichloroethylene and its metabolites, trichloroacetate and dichloroacetate., Environ. Health Perspect. (2000) 241–59.

[43] A. El-Aty, M. Ibrahim, Influence of chlorine on algae as precursors for trihalomethane and haloacetic acid production, World Appl. Sci. …. 6 (2009) 1215–1220.

[44] J.T. Lennon, S.K. Hamilton, M.E. Muscarella, A.S. Grandy, K. Wickings, S.E. Jones, A source of terrestrial organic carbon to investigate the browning of aquatic ecosystems., PLoS One. 8 (2013) e75771.

[45] A.W. Zularisam, A.F. Ismail, M.R. Salim, M. Sakinah, H. Ozaki, The effects of natural organic matter (NOM) fractions on fouling characteristics and flux recovery of ultrafiltration membranes, Desalination. 212 (2007) 191–208.

[46] A. Piccolo, Humic substances in terrestrial ecosystems, Elsevier, 1996.

[47] L. Aguilar, L.J. Thibodeaux, Kinetics of peat soil dissolved organic carbon release from bed sediment to water. Part 1. Laboratory simulation, Chemosphere. 58 (2005) 1309–1318.

[48] D.A. Reckhow, P.L.S. Rees, G. Makdissy, D. Bryan, Management of Water Supplies for Control of Disinfection Byproduct Precursors, 2005.

[49] K. Kalbitz, D. Schwesig, J. Schmerwitz, K. Kaiser, L. Haumaier, B. Glaser, R. Ellerbrock, P. Leinweber, Changes in properties of soil-derived dissolved organic matter induced by biodegradation, Soil Biol. Biochem. 35 (2003) 1129–1142.

[50] A.T. Chow, F. Guo, S. Gao, R.S. Breuer, Size and XAD fractionations of trihalomethane precursors from soils, Chemosphere. 62 (2006) 1636–1646.

[51] M. Kitis, T. Karanfil, A. Wigton, J.E. Kilduff, Probing reactivity of dissolved organic matter for disinfection by- product formation using XAD-8 resin adsorption and ultrafiltration, Water Res. 36 (2002) 3834–3848.

[52] AWWARF, J.-P. Croue, G. V. Korshin, M.M. Benjamin, Characterization of Natural Organic Matter in Drinking Water, (2000) 324.

[53] L.A. Rossman, R.A. Brown, P.C. Singer, J.R. Nuckols, DBP formation kinetics in a simulated distribution system, Water Res. 35 (2001) 3483–3489.

[54] Z. Wang, C.M. Hessler, Z. Xue, Y. Seo, The role of extracellular polymeric substances on the sorption of natural organic matter, Water Res. 46 (2012) 1052–1060.

[55] Z. Wang, J. Kim, Y. Seo, Influence of bacterial extracellular polymeric substances on the formation of carbonaceous and nitrogenous disinfection byproducts, Environ. Sci. Technol. 46 (2012) 11361–11369.

[56] J.-J. Wang, X. Liu, W. Ng, J.-W. Xiao, A.T. Chow, P.K. Wong, Disinfection byproduct formation from chlorination of pure bacterial cells and pipeline biofilms, Water Res. 47 (2013) 2701–2709.

[57] Y. Penru, F.X. Simon, A.R. Guastalli, S. Esplugas, J. Llorens, S. Baig, Characterization of natural organic matter from Mediterranean coastal seawater, J. Water Supply Res. Technol. 62 (2013) 42–51.

[58] H.-W. Yu, S.-G. Oh, I.S. Kim, I. Pepper, S. Snyder, A. Jang, Formation and speciation of haloacetic acids in seawater desalination using chlorine dioxide as disinfectant, J. Ind. Eng. Chem. 26 (2015) 193–201.

[59] H.W. Yu, S.G. Oh, I.S. Kim, I. Pepper, S. Snyder, A. Jang, Formation and speciation of haloacetic acids in seawater desalination using chlorine dioxide as disinfectant, J. Ind. Eng. Chem. 26 (2015) 193–201.

[60] V. Kanokkantapong, T.F. Marhaba, B. Panyapinyophol, P. Pavasant, FTIR evaluation of functional groups involved in the formation of haloacetic acids during the chlorination of raw water, J. Hazard. Mater. 136 (2006) 188–196.

[61] B. Li, J. Qu, H. Liu, C. Hu, Effects of copper(II) and copper oxides on THMs formation in copper pipe, Chemosphere. 68 (2007) 2153–2160.

[62] R. Liu, C. Tian, C. Hu, Z. Qi, H. Liu, J. Qu, Effects of bromide on the formation and transformation of disinfection by-products during chlorination and chloramination, Sci. Total Environ. 625 (2018) 252–261.

[63] H. Fakour, S.L. Lo, Formation of trihalomethanes as disinfection byproducts in herbal spa pools, Sci. Rep. 8 (2018) 1–11.

[64] C.-Y. Chang, Y.-H. Hsieh, S.-S. Hsu, P.-Y. Hu, K.-H. Wang, The formation of disinfection by-products in water treated with chlorine dioxide, J. Hazard. Mater. 79 (2000) 89–102.

[65] H.C. Hong, M.H. Wong, Y. Liang, Amino Acids as Precursors of Trihalomethane and Haloacetic Acid Formation During Chlorination, Arch. Environ. Contam. Toxicol. 56 (2009) 638–645.

CHAPTER 8

SUMMARY AND CONCLUSIONS

Chapter 8

Summary and Conclusions

Chlorination of natural water was inextricably associated with the formation of toxic DBPs such as THMs and HAAs. Treatment with chlorine dioxide is associated with a smaller amount of THMs and HAAs, however, the formation of ClO_2^- and ClO_3^- introduced additional concerns. Several key issues were investigated in this work through field monitoring and experimental studies on the formation of THMs and HAAs. The conclusions of this dissertation were elaborated separately in chapters 4, 5, 6 and 7, and summarised again in this chapter.

8.1 General Conclusions

- Distinct variations in chlorine demand and total THMs formation were observed for the three water sources studied. Water quality descriptors such as pH, temperature, bromide, UV_{254} etc. failed to establish a strong correlation with chlorine demand and trihalomethanes formation potential due to the numerous simultaneous occurring reactions. Chlorine demand in conjunction with other water quality descriptors seemed to be a better alternative surrogate to predict the THM yield capacity of the water.
- The TRC values at the MAPS outfall were within the pollution control board stipulated value of 0.5 mg/L. There was a reduction of about 25% for FRC and 8% for TRC at the mixing point as compared to the values obtained at the outfall discharge. The present low dose chlorination adopted at MAPS seawater cooling system not only serves the operational requirement of

biofouling control but also comply with the environmental stipulation of Cl_2 residual a well as trihalomethanes.

- The TTHM formation rate followed a very high initial rate and after 5 h of chlorination subsidized considerably. The overall formation of different THM species followed the order: $CHCl_2Br$ (<1%) < $CHClBr_2$ (<2%) < $CHBr_3$ (96-98%).
- Disinfection by-products were higher in open reservoir samples as compared to Palar river samples which suggested that chlorination of open storage water might lead to a higher health risk. DOC content and UVA_{254} did not correlate well with trihalomethanes formation for both the water types and thus could not be taken as a surrogate parameter for prediction of trihalomethanes formation potential of the studied freshwater.
- The extent of bromide present in the raw water must be taken into consideration if chlorine has to be used for disinfection and more so if it is in close proximity to coastal areas because of the higher level of toxicity of brominated THMs.
- In general, the order of THMs formation potential of three water sources was RSR > SWR > RVR for chlorination whereas it was SWR > RSR > RVR for ClO_2 treatment. Total DBPs formed were always less for ClO_2 treatment as compared to that formed during chlorination irrespective of water type.
- HAAs were observed to be more readily formed than THMs during ClO_2 treatment, and the order was opposite for chlorination.
- For river and reservoir water (fresh water), bromine incorporation percentage for THMs and HAAs were higher during ClO_2 treatment than chlorine

treatment. The propensity of bromine incorporation was observed to be more in THMs than HAAs.

- For both Cl_2 and ClO_2 treatment, di-HAAs were dominant and more readily formed than Tri-HAAs followed by a small quantity of mono-HAAs regardless of source water type.
- A significant amount of chlorate could be inadvertently introduced due to the contamination of the hypochlorite feedstock.
- For ClO_2 treatment, a higher yield of THMs and HAAs was observed for the individual fractions compared to the total IOC and EOC could not be explained with the present information on the structural contribution and disinfectant reactivity
- Algal EOC was associated with higher THMs as compared to IOC, and IOC was associated with higher HAAs formation indicating different precursor composition of IOC and EOC.
- Four HAAs species; DCAA, DBAA, TCAA, and BCAA dominated the total HAAs during both chlorine and chlorine dioxide treatment of AOM.
- Among the algal, bacterial and soil organic matter studied, THMs and HAAs formed per mg carbon was highest for soil.
- Among HPO, TPI, and HPI of soil organic matter, SOCA-TPI and SOCB-HPO showed highest SHAAFPs for both Cl_2 and ClO_2 treatment which showed that the precursor responsible for the formation of THMs may be different to HAAs precursor, and the reactivity of the chlorine dioxide with the HAAs precursor is more prominent than that with THMs precursor for soil organic carbon.

- Since the overall THMs formation was low for the soil organic, its speciation behavior is of less important during ClO_2 treatment.
- For bacterial derived organic matter, overall, the order of STHMFPs for chlorination was; BEOC: TPI > HPI > HPO, BIOC: HPO > HPI > TPI and the order of SHAAFPs was BEOC: HPI > TPI > HPO, BIOC: HPI > HPO > TPI. The order of DBPs formation was TCM > DCAA > TCAA > BDCM > DBCM both for chlorine and chlorine dioxide treatment.
- The average value of DCAA to TCAA ratio for the bacterial-derived organic matter was 2.24:1 for chlorine and 6.3:1 for chlorine dioxide treatment. This indicated that the precursor involved for TCAA formation was less reactive to ClO_2 than $Cl_{2.}$
- ClO_2 treatment of bacterial organic matter generates a considerable amount of THMs which was least formed in the case of algal and soil organic matter.
- Though organic matter derived from all the sources such as algal, bacterial and soil organic has significant potential for the CBPs formation, soil-derived organic matter showed the highest formation potential and to be considered as a part of DBP control plan. Since algal organic matter showed high consumption of ClO_2 than Cl_2, application of chlorine dioxide to natural water containing high algal content or during the event such as algal bloom has to be checked carefully for the availability of the desired residual.

8.2 Implications

The work demonstrated that chlorine demand and total THMs formation varied widely with regard to type of water source and water quality descriptors such as pH, temperature, and bromide. All these parameters failed to establish a strong correlation with chlorine demand and trihalomethanes formation potential due to the numerous simultaneous occurring reactions thus, making it difficult to derive a universal predictive model for CBPs formation. The study confirmed that the present the discharge of Cl_2 residual and trihalomethanes in the MAPS outfall discharge were within the environmental stipulation during the low dose chlorination regime adopted for biofouling control at MAPS seawater cooling system. The work furthered the understanding on the effect of bromide in fresh water source on the formation of brominated THMs and HAAs during Chlorine and chlorine dioxide treatment and also demonstrated that the water quality most likely to get deteriorated upon its storage in open reservoir with respect to disinfection efficiency and DBPs formation. The results of the research suggest that the formation of chlorate and chlorite must be thoroughly studied in case of chlorine dioxide treatment of natural water. The investigations carried out on the algal, bacterial and soil organic matter contribution to aquatic system and their relativity towards chlorine and chlorine dioxide for DBPs formation would help to trace the reactivity of different organic constituent with their origin and would also aid to better management of DBPs controls strategies

8.3 Future Scope

The consequence of lack of correlation between physicochemical properties and DBP formation in a temporal and spatial scale necessitates the identification of a more reliable combination of determinants for universal DBPs predictions. Recommendation for further research broadly includes characterization of NOM to a deeper level, the fate of CBPs post-formation (post-discharge in case of cooling water effluent), and more studies on real water from different geographical region to reduce data heterogeneity and identification of new by-products formed during disinfection other than chlorination. Moreover, the alterations in structural and chemical compositions of DOM during chlorination remain unclear. Studies on the interactions of chlorine and chlorine dioxide with DOM during water treatment as well as the characteristics of DOM is essential to understand the formation mechanisms of DBPs better.

******