RGC Ref. No.:
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(please insert ref. above)

RESEARCH GRANTS COUNCIL
COMPETITIVE RESEARCH FUNDING SCHEMES FOR
THE LOCAL SELF-FINANCING DEGREE SECTOR

FACULTY DEVELOPMENT SCHEME (FDS)

Completion Report
(for completed projects only)

Submission Deadlines: *1. Auditor's report with unspent balance, if any: within **six** months of the approved project completion date.*
*2. Completion report: within **12** months of the approved project completion date.*

Part A: The Project and Investigator(s)

1. Project Title

Formation, fate and toxicity of chlorination byproducts generated in seawater desalination by reverse osmosis

2. Investigator(s) and Academic Department(s) / Unit(s) Involved

Research Team	Name / Post	Unit / Department / Institution
Principal Investigator	WANG Chao / Assistant Professor	Faculty of Science and Technology / Technological and Higher Education Institute (THEi) of Hong Kong
Co-Investigator(s)	SHANG Chii / Professor LEE Kin Man Amazon / Professor	Department of Civil & Environmental Engineering / HKUST Faculty of Science and Technology / Technological and Higher Education Institute (THEi) of Hong Kong
Others		

3. Project Duration

	Original	Revised	Date of RGC / Institution Approval *(must be quoted)*

Project Start Date	1 Jan 2016	NA	NA
Project Completion Date	30 Jun 2018	31 Dec 2018	22 Feb 2018
Duration *(in month)*	30	36	22 Feb 2018
Deadline for Submission of Completion Report	30 Jun 2019	31 Dec 2019	22 Feb 2018

Part B: The Final Report

5. Project Objectives

5.1 Objectives as per original application

1. Assessing the formation of chlorination byproducts during the chlorination pretreatment process of seawater desalination by RO;
2. Evaluating the impacts of operating conditions and seawater characteristics on the formation of chlorination byproducts during the chlorination pretreatment process of seawater desalination by RO;
3. Investigating the fate of chlorination byproducts during seawater desalination by RO;
4. Assessing the adverse effects of chlorination byproducts in brine to the representative marine organism.

5.2 Revised objectives

Date of approval from the RGC: NA

Reasons for the change: NA

5.3 Realisation of the objectives
(Maximum 1 page; please state how and to what extent the project objectives have been achieved; give reasons for under-achievements and outline attempts to overcome problems, if any)

All objectives of the project have been achieved. **For Objective 1**, chlorinated, brominated, iodinated and other new disinfection byproducts (DBPs) formed during the process of chlorination pretreatment under conditions simulating RO desalination treatment have been detected and identified. Concentrations of monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), dichlorobromoacetic acid (DCBAA), chloroiodoacetic acid (CIAA), dibromochloroacetic acid (DBCAA), bromoiodoacetic acid (BIAA), tribromoacetic acid (TBAA), diiodoacetic acid (DIAA), total organic iodine (TOI) and unknown DBPs have been measured. TBAA was the most abundant HAA species of the total HAA formation and DBAA ranked the second. 12 volatile DBPs and 11 HAAs were detected under all operating conditions (chlorine dosage, contact time, pH and temperature) in chlorination pretreatment of seawater desalination. TBM, TBAA, DBCAN and DBAL concentrations dominated in their groups (THMs, HAAs, N-DBPs and HALs). Besides, trace amounts of iodinated DBPs were detected at ng/L levels. Furthermore, low total organic chlorine (TOCl) concentrations and high total organic bromine (TOBr) concentrations were detected under different conditions, while TOI was not detected. In most of the conditions, total organic halogen (TOX) concentrations were higher than the total detected DBP concentrations. At a baseline condition of pH = 8, seawater TOC = 0.5 mg/L, temperature = 23 °C, contact time = 2 hours, and chlorine dosage = 2 mg/L as Cl_2, 16 chlorinated and brominated DBPs were selectively detected by ESI-tqMS PIS method, including 14 unknowns containing 2 halogens and 2 unknowns containing 3 halogens. A novel technique, FT-ICR-MS has been applied to assess the formation of new DBPs. **For Objective 2**, the impacts of operating conditions and seawater characteristics on the formation of chlorination byproducts during the chlorination pretreatment process of seawater desalination by RO have been evaluated. With increasing chorine dosages from 2 mg/L to 10 mg/L, total THMs formation first increased from 26.7 μg/L to 33.9 μg/L and remained constant, while HAAs formation increased slightly from 16.1 μg/L to 16.8 μg/L and to 30.3 μg/L subsequently, nitrogen-containing DBPs (N-DBPs, including HANs, HNMs and HAcAm) formation increased from 0.8 μg/L to 1.3 μg/L, and HALs formation first increased from 0.9 μg/L to 1.5 μg/L and then decreased to 1.0 μg/L. With increasing contact time from 0.5 hour to 3 hours, THMs formation first increased from 18.8 μg/L to 26.7 μg/L and further increased to 33.2 μg/L, while HAAs formation increased first from 10.0 μg/L to 16.1 μg/L and to 18.4 μg/L, N-DBPs formation increased from 0.5 μg/L to 0.8 μg/L and to 0.9 μg/L, and HALs kept decreasing from 1.5 μg/L to 0.9 μg/L and further to 0.5 μg/L. With increasing pH from 6.5 to 10, THMs formation first increased from 21.0 μg/L to 26.7 μg/L and later decreased to 22.3 μg/L, while HAAs formation kept decreasing from 20.1 μg/L to 16.1 μg/L and to 12.4 μg/L, N-DBPs formation kept decreasing from 0.9 μg/L to 0.8 μg/L and then to 0.4 μg/L, and HALs formation decreased from 2.7 μg/L to 0.9 μg/L and to 0.2 μg/L. With increasing temperature from 17 °C to 29 °C, THMs formation first remained at around 26 μg/L and subsequently increased to 33.7 μg/L, while HAAs formation increased firstly from 14.8 μg/L to 16.1 μg/L and decreased to 15.7 μg/L subsequently, N-DBPs formation firstly increased from 0.6 μg/L to 0.8 μg/L and remained constant, and HALs formation kept decreasing from 1.3 μg/L to 0.9 μg/L and to 0.4 μg/L. Chlorination pretreatment of seawater upon intake in seawater desalination systems changes the structures of seawater organic matter (SOM) and forms DBPs. This part of the study investigated the changes in specific ultraviolet absorbance (SUVA) and fluorescence excitation emission matrix (FEEM) of SOM, and their correlations with the DBPs/TOX formation in seawater chlorination pretreatment under different conditions. Most SUVA values and all FEEM values decreased, suggesting that SOM was degraded in chlorination. Changes in SUVA/FEEM of SOM correlated with the DBPs/TOX formation strongly at different chlorine dosages and temperatures, and moderately at different contact times. **For Objective 3**, in RO permeate, the total DBP concentrations under preformed chloramination is lower than the other three pretreatment strategies, and the difference among the other three pretreatment strategies is insignificant in the total DBP concentrations. The regulated DBPs (e.g. THM4, HAA5, DBAN) are at levels below their respective maximum contamination levels (MCLs), but other DBPs (e.g. HAAs, BCAN) with comparable concentrations are not regulated. In RO brine, only six out of seventeen DBPs have been studied for their effects to aquatic organisms, and the concentrations of these six DBPs (e.g. TBM, DBCM, DCBM, MBAA, TCAA, DCAA) are far below their respective thresholds of the known effects. However, these six DBPs only account for approximately 30% of the total DBP concentrations. Comparing different pretreatment strategies from the perspectives of the other eleven DBPs, the same trend as mentioned in total DBP concentrations occurs. On a molar concentration basis, HAAs, following by THMs, are the predominant DBPs. When weighted by measures of toxic potency, nitrogenous DBPs (e.g. DBAcAm and DBAN) and, to a lesser degree, HAAs (e.g. TBAA) become the important contributors to the total calculated cytotoxicity. **For Objective 4**, the representative marine algae *Skeletonema costatum* showed no acute response to the brine containing the highest concentrations of DBPs. But increasing chlorine dosages or decreasing pHs increased more significantly the integrated cyto- and geno-toxicity than the DBP concentrations. Increasing contact times and temperatures also increased the DBP concentrations and integrated genotoxicity. However, the integrated cytotoxicity did not change with increasing contact times, and decreased with increasing temperatures. 1 paper is published, 4 more papers are to be published in 2020. The research items were presented in 4 international conferences.

5.4 Summary of objectives addressed to date

Objectives *(as per 5.1/5.2 above)*	**Addressed** *(please tick)*	**Percentage Achieved** *(please estimate)*
1. Assessing the formation of chlorination byproducts during the chlorination pretreatment process of seawater desalination by RO;	√	100%
2. Evaluating the impacts of operating conditions and seawater characteristics on the formation of chlorination byproducts during the chlorination pretreatment process of seawater desalination by RO;	√	100%
3. Investigating the fate of chlorination byproducts during seawater desalination by RO;	√	100%
4. Assessing the adverse effects of chlorination byproducts in brine to the representative marine organism.	√	100%

6. Research Outcome

6.1 Major findings and research outcome
(Maximum 1 page; please make reference to Part C where necessary)

The major findings obtained from this study have formulated 1 prestigious journal paper (journal paper #1) and 4 conference presentations (conference presentations #1-4) in two outstanding international conferences so far. We are also working on another 4 journal papers (journal paper #2-5). This study provided training of one research assistant. This study also involved close collaboration between THEi and HKUST. The specific major findings are:

A dialysis method was established in this project to analyze adsorbable organic halogens formed in seawater chlorination (journal paper #1). And the total DBP concentrations increase with increasing chlorine dosages, contact times and temperatures, but decrease with increasing pHs. And their concentrations formed in the process are well correlated with the changes in seawater organic matter properties. The brine discharged from seawater desalination contains higher concentrations of DBPs and was proved to possess higher cyto- and geno- toxicities. There are many new unknown DBPs formed in the seawater desalination, and those unknown DBPs can pass RO membrane and possess potential threat to human health. Seawater chloramination can reduce the DBPs formation and toxicity, but may possess larger ecological impacts in brine than seawater chlorination (conference presentation #1-4 and journal paper #2-5).

6.2 Potential for further development of the research and the proposed course of action *(Maximum half a page)*

In this project, we have observed that DBPs formation increases with increasing chlorine dosages, contact times and temperatures, but decreases with increasing pHs. To balance the disinfection power of seawater and byproduct formation at different situations, increasing contact time instead of chlorine dosage is a better option, since increasing contact time has a less significant impact on DBP formation and integrated toxicities. In addition, the DBP formation and their integrated calculated toxicities are in good correlation with the changes in seawater organic matter properties. Therefore, we are planning to develop new and simple spectrophotometric methods to predict the DBP formation during chlorination to replace the conventional and complicated gas chromatograph methods.

In addition, with better understanding of the unknown DBP formation, their pathways and their fate in the desalination plant, we can have a better assessment of the unknown DBPs to drinking water, when desalination is used as the alternative potable water sources.

7. Layman's Summary

(Describe <u>in layman's language</u> the nature, significance and value of the research project, in no more than 200 words)

Seawater desalination using reverse osmosis (RO) technology has become an important way of producing freshwater to meet the growing water demands worldwide. Hong Kong has also proposed to build a RO seawater desalination plant to provide about 5% of its fresh water supply. In RO desalination plants, chlorination prior to filtration for preventing the bio-fouling on intake structures and membranes will inevitably lead to the generation of chlorination byproducts that pose potential health, aesthetic and ecological

risks. Less is known on chlorination byproducts formation in seawater desalination by RO.

In this study, we provided a breakthrough in filling the knowledge gap of the known and unknown DBPs formation under different operating conditions including chlorine dosages, contact times and chlorination modes, and evaluated the changes in seawater organic matter properties and the toxicities after chlorination. More importantly, we have established a method to correlate their concentrations and toxicities with the changes in seawater organic matter properties. The improved understanding of the formation of DBPs in seawater chlorination is beneficial to the monitoring and control of byproducts formed in the process. It is also of significant scientific merit in understanding the chemistry of the interactions among chlorine, bromine, and seawater organic matters.

Part C: Research Output

8. Peer-Reviewed Journal Publication(s) Arising Directly From This Research Project

(Please attach a copy of the publication and/or the letter of acceptance if not yet submitted in the previous progress report(s). All listed publications must acknowledge RGC's funding support by quoting the specific grant reference.)

The Latest Status of Publications				Author(s) *(denote the corresponding author with an asterisk*)*	Title and Journal / Book *(with the volume, pages and other necessary publishing details specified)*	Submitted to RGC *(indicate the year ending of the relevant progress report)*	Attached to this Report *(Yes or No)*	Acknowledged the Support of RGC *(Yes or No)*	Accessible from the Institutional Repository *(Yes or No)*
Year of Publication	**Year of Acceptance** *(For paper accepted but not yet published)*	**Under Review**	**Under Preparation** *(optional)*						
2018				**Jiajian Liu[1], Li Ling[1], Yi Li, Chao Wang*, Chii Shang***	**Title: A modified method of high molecular weight adsorbable organic chlorine measurement in saline water: Dialysis pretreatment** **Science of the Total Environment, 639, 258-262.**	**31 Dec 2017**	**Yes**	**Yes**	**Yes**
			√	**Jiajian Liu[1], Li Ling[1], Qianyuan Wu, Chao Wang*, Chii Shang***	**Title: DBP formation in seawater chlorination** **Water Research**	**No**	**No**	**Yes**	**NA**
			√	**Jiajian Liu[1], Li Ling[1], Chao Wang*, Chii Shang***	**Title: DBP formation in seawater chloramination** **Science of the Total Environment**	**No**	**No**	**Yes**	**NA**
			√	**Jiajian Liu[1], Li Ling[1], Chao**	**Title: DBP occurrence and cytotoxicit**	**No**	**No**	**Yes**	**NA**

				Wang*, Chii Shang*	**y in permeate and brine from RO desalination by chlor(am)ination pretreatment Water Research**				
			√	**Jiajian Liu[1], Li Ling[1], Yingying Xiang, Chao Wang*, Chii Shang***	**Title: New DBP formation in the permeate from RO desalination: A study using FT-ICR-MS Water Research**	**No**	**No**	**Yes**	**NA**

9. Recognized International Conference(s) In Which Paper(s) Related To This Research Project Was / Were Delivered

(Please attach a copy of each conference abstract)

Month / Year / Place	**Title**	**Conference Name**	**Submitted to RGC** *(indicate the year ending of the relevant progress report)*	**Attached to this Report** *(Yes or No)*	**Acknowledged the Support of RGC** *(Yes or No)*	**Accessible from the Institutional Repository** *(Yes or No)*
05/2018/Beijing, China	**Integrated cyto- and geno- toxicity caused by DBPs formed in seawater chlorination**	**2nd Disinfection and Disinfection By-Products Conference**	**31 Dec 2017**	**No**	**Yes**	**No**
05/2018/Beijing, China	**Correlations between structural changes of seawater organic matter and DBP formation in seawater chlorination**	**2nd Disinfection and Disinfection By-Products Conference**	**31 Dec 2017**	**No**	**Yes**	**No**
07-08/ 2017/ Mount Holyoke College South Hadley, MA, USA	**Property changes in seawater natural organic matter during seawater chlorination and their correlations with disinfection by-products formation**	**Gordon Research Conference on DBPs 2017 — Disinfection 2100: Linking Engineering, Chemistry, Toxicology and Epidemiology to Reduce Exposure to Toxicity Drivers While Curtailing Pathogens**	**31 Dec 2016**	**No**	**Yes**	**No**

07-08/ 2017/ Mount Holyoke College South Hadley, MA, USA	**TOX measurement in high salinity water: A new pretreatment method**	**Gordon Research Conference on DBPs 2017 — Disinfection 2100: Linking Engineering, Chemistry, Toxicology and Epidemiology to Reduce Exposure to Toxicity Drivers While Curtailing Pathogens**	**31 Dec 2016**	**No**	**Yes**	**No**

10. Whether Research Experience And New Knowledge Has Been Transferred / Has Contributed To Teaching And Learning
(Please elaborate)

For the topic of Water Treatment in the Course "Introduction to Environmental Engineering", PI used the results from this study to explain the risks caused by DBPs generated during seawater desalination by Reverse Osmosis.

11. Student(s) Trained
(Please attach a copy of the title page of the thesis)

Name	Degree Registered for	Date of Registration	Date of Thesis Submission / Graduation
Nil	Nil	Nil	Nil

12. Other Impact
(e.g. award of patents or prizes, collaboration with other research institutions, technology transfer, teaching enhancement, etc.)

Some experiment work using UPLC with ESI-QTOF-MS and UPLC with ESI-tqMS was conducted in the Environmental Lab of HKUST. This will promote the collaboration between THEi and HKUST.

13. Statistics on Research Outputs

	Peer-reviewed Journal Publications	Conference Papers	Scholarly Books, Monographs and Chapters	Patents Awarded	Other Research Outputs (please specify)	
No. of outputs arising directly from this research project	1 published, and 4 in preparation	4	NA	NA	Type	No.
					NA	NA

14. Public Access Of Completion Report

(Please specify the information, if any, that cannot be provided for public access and give the reasons.)

Information that Cannot Be Provided for Public Access	Reasons
NA	NA