

ABSTRACT

This doctoral thesis investigates biogenic emissions of selected Very Short-lived Species (VSLS) bromocarbons like bromoform (CHBr_3), dibromomethane (CH_2Br_2), dibromochloromethane (CHBr_2Cl) and selected chlorocarbons like chloroform (CHCl_3) and tetrachloroethylene (C_2Cl_4) from different environments through ground and a shipborne field campaign. Brominated halocarbon is an atmospheric trace gas and a major source of atmospheric bromine. Recent estimates of brominated halocarbon sources and sinks indicate anthropogenic sources to be negligible. The major source of atmospheric brominated compounds is believed to be from marine especially coastal area. The production pathways of brominated compounds in the ocean are, however, poorly understood. Measurements were made using a μ -Dirac, which is a self-built instrument, consisting of a continuously operating gas chromatograph (GC), equipped with electron capture detector (ECD). This system was used for 3 ground field long term measurement in the coastal and tropical area to measure the air concentrations and the atmospheric dry gas mole fractions of the selected VSLS bromocarbons. The correlations plot of the mixing ratios between well correlated bromocarbons VSLS suggests that the bromocarbons species were emitted from biogenic or anthropogenic sources for both long term and short term measurement.

Laboratory experiments were also conducted to test the hypothesis that bromocarbons produced in the ocean's surface water are by marine plant like seaweeds, instead of direct biological production by phytoplankton or bacteria. The experiments were conducted on 7 types of seaweeds differentiated by its groups red, brown and green. A commercial purge and trap connected to a commercial GC-ECD was used to measure the VSLS halocarbons in seawater. The lab production studies showed diurnal cycle in the

water samples. The concentration increased with increasing light intensity and sea surface temperature (SST) showing the highest concentration level at mid-day. The production of bromocarbons VSLs observed in all experiments kept in the sunlight was five times higher than the production from incubations kept in the dark. This strongly indicates photochemical production with no direct influence by biota. The mean photochemical production rate of the bromocarbons VSLs from each experiment was 1 to 137 pmol per g⁻¹ FW⁻¹ h⁻¹, where, the red seaweeds was the highest producer followed by brown and green. The bromoperoxidase (BPO) enzyme was also extracted from all types of seaweeds, and result shows high BPO activity in red followed with brown and green seaweeds. From these results, it can be concluded that the photochemical production of bromocarbons VSLs plays an important role that may be dominant, in contributing to the tropospheric and stratospheric ozone depletion over the tropical region.

ABSTRAK

Tesis doctoral ini menyelidik pembebasan biogenic Spesies dengan Hayat Amat Pendek (VSLS) bromokarbon terpilih seperti bromoform (CHBr_3), dibromometana (CH_2Br_2), dibromoklorometana (CHBr_2Cl) dan klorokarbon terpilih seperti kloroform (CHCl_3) dan tetrakloroetilena (C_2Cl_4) daripada persekitaran yang berbeza melalui pensampelan di daratan dan lautan. Halokarbon berbromin merupakan suatu gas surih di atmosfera dan sumber utama bromine atmosfera. Anggaran terkini bagi sumber dan sinki halocarbon berbromin menunjukkan bahawa sumber antropogenik boleh diabaikan. Sumber utama sebatian-sebatian berbromin di atmosfera adalah dipercayai datangnya daripada lautan, terutama kawasan persisiran pantai. Walau bagaimanapun, laluan bagi penghasilan sebatian berbromin dalam lautan masih belum difahami sepenuhnya. Pengukuran dibuat dengan menggunakan μ -Dirac, iaitu suatu peralatan yang dibina sendiri, yang terdiri daripada kromatograf gas (GC) yang beroperasi secara berterusan dan dilengkapi dengan pengesan penangkap electron (ECD). Sistem ini digunakan untuk 3 pengukuran jangka panjang daratan di kawasan persisiran pantai tropika, iaitu untuk mengukur kepekatan udara dan pecahan mol gas kering atmosfera VSLS bromokarbon terpilih. Plot korelasi nisbah percampuran yang memberikan korelasi yang baik di antara bromokarbon VSLS menyimpulkan bahawa spesies bromokarbon dibebaskan daripada sumber biogenic atau antropogenik bagi kedua-dua pengukuran jangka pendek atau jangka panjang.

Eksperimen di makmal juga dijalankan bagi menguji hipotesis bahawa bromokarbon yang dihasilkan dalam air permukaan laut adalah daripada tumbuhan marin seperti rumput laut, dan tidak melalui penghasilan biologi terus oleh fitoplankton atau bacteria. Eksperimen telah dilakukan ke atas 7 jenis rumput laut yang dibezakan oleh kumpulan, iaitu merah, coklat dan hijau. Suatu peralatan singkir dan perangkap komersial

yang disambungkan kepada suatu GC-ECD komersial digunakan untuk mengukur halocarbon VSLS yang terdapat dalam air laut. Kajian penghasilan dalam makmal menunjukkan kitar diurnal dalam sampel air. Kepekatan meningkat bersama peningkatan keamatan cahaya dan suhu permukaan laut (SST) dengan menunjukkan aras kepekatan tertinggi pada tengah hari. Penghasilan VSLS bromokarbon yang diperhatikan dalam semua eksperimen yang didedahkan kepada cahaya matahari adalah lima kali lebih tinggi daripada penghasilan daripada eksperimen yang disimpan dalam gelap. Ini dengan jelas menunjukkan penghasilan fotokimia tanpa pengaruh langsung daripada biota. Min bagi kadar penghasilan fotokimia VSLS bromokarbon daripada setiap eksperimen adalah di antara 1 kepada 137 pmol per $\text{g}^{-1} \text{FW}^{-1} \text{h}^{-1}$, di mana rumput laut merah merupakan pengeluar tertinggi, diikuti oleh rumput laut coklat dan hijau. Enzim bromoperoksidase (BPO) juga telah diekstrak daripada semua jenis rumput laut, dan keputusan menunjukkan keaktifan BPO yang tinggi bagi rumput laut jenis merah, diikuti oleh coklat dan hijau. Daripada hasil kajian ini dapat disimpulkan bahawa penghasilan fotokimia VSLS bromokarbon memainkan peranan penting yang mungkin juga dominan dalam menyumbang terhadap penipisan ozon troposfera dan stratosfera di kawasan tropika.

ACKNOWLEDGEMENT

First and above all, I praise God, the almighty for providing me this opportunity and granting me the capability to finished this thesis successfully. I am deeply indepted to my supervisor Professor Dr. Mhd. Radzi bin Abas and Professor Dr. Noorsaadah Abd. Rahman, whose accepted me as their PhD student and encouraged, advised, support and guidance me throughout this thesis period. And not least, my internal advisors Prof Dr. Amru Nasrulhaq Boyce and Prof Dr. Phang Siew Moi for guided and advised me on biochemistry work and the used of their laboratory facilities. I am also grateful to University of Malaya for the scholarship and research grant which enable me to carry out this PhD program,

I also want to express my deep thanks to the members of the advisor committee from the department of chemistry, atmospheric chemistry group University of Cambridge; Professor Dr. John Pyle, Dr. Neil Harris, Dr. Andrew Robinson and Mr. Bryan Gostlow and from the school of environmental sciences University of East Anglia; Professor Dr. William Sturges, Dr. David Oram, Dr. Graham Mills and Ms. Emma Leedham for their excellent advises and detailed review during the preparation of this thesis.

Special thanks to my lab mates especially; Dr. Tay, Aaina, Aalia, Dr. Yean Kee, Norashikin, Dr. Chee, Fiona, Jebry and Syed and at University of Cambridge; Matt and Iq for brilliant ideas and suggestion in atmospheric chemistry work. Last but not least, my deepest appreciation to my wife Sakinah Mohd Alauddin, children and family members for their patience and supporting me the many hours I spent preparing this thesis and my field works.

CONTENTS

ABSTRACT	ii
ABSTRAK	iv
ACKNOWLEDGEMENT	vi
CONTENTS	vii
LIST OF FIGURES	xiv
LIST OF TABLES	xxi
LIST OF ABBREVIATIONS	xxiii
LIST OF MOLECULAR FORMULAE	xxv
LIST OF SYMBOLS	xxvii
LIST OF UNITS	xxviii
1 General Introduction	
1.1 General introduction	2
1.2 Ozone production and destruction	5
1.2.1 Ozone in the stratosphere	5
1.2.2 Ozone in troposphere	8
1.3 Halocarbons	11
1.3.1 Basic chemistry of halocarbons	12
1.3.2 Ozone depletion mechanism due to halogens	13
1.4 Lifetimes of halocarbons in the atmosphere	15

1.4.1	Long-lived and Short-lived halocarbons	16
1.4.2	Very short-lived halocarbon in the atmosphere	23
1.5	Distributions of VSLS in the troposphere and stratosphere	24
1.6	Sources and sinks of VSLS	31
1.6.1	Halocarbons sources and transport	31
1.6.2	Transport to the troposphere and stratosphere	34
1.6.3	VSLS transport from surface to Tropical tropopause layer (TTL)	35
1.6.4	VSLS transport from TTL to stratosphere	37
1.7	Sources of VSLS	38
1.7.1	Anthropogenic	40
1.7.2	Biogenic	41
1.8	Goal of the study	43
1.9	References	44
2	Analytical methodology	
2.1	Introduction	60
2.2	Method for halocarbons measurement	61
2.2.1	Liquid-liquid extraction	62
2.2.2	Head space	63
2.2.3	Purge and Trap	64
2.3	Instrumentation setup	67
2.3.1	VSLS halocarbons measurement	67
2.3.1.1	Micro-Dirac Gas chromatography (μ -Dirac GC)	67
2.3.1.1.1	Instrument description	68
2.3.1.1.1.1	Inlet manifold	70

2.3.1.1.1.2	Sample adsorption and desorption system	71
2.3.1.1.1.3	Temperature programmed column	72
2.3.1.1.1.4	Helium pressure controller	74
2.3.1.1.1.5	Detection system	74
2.3.1.1.1.6	Nitrogen pressure controller	75
2.3.1.1.1.7	Back pressure controller	76
2.4	μ -Dirac performance	76
2.4.1	Calibration	76
2.4.2	Accuracy and precision	77
2.5	Flasks sampling	78
2.5.1	Cruise sampling and measurements	80
2.6	Production rate analysis	80
2.6.1	Seaweeds collection	80
2.6.2	Analytical instrumentation	80
2.6.2.1	Purge and trap system	81
2.6.2.2	Standard	83
2.6.2.3	Calibration	84
2.6.3	Accuracy and precision	89
2.6.4	Blank	91
2.6.5	Purge and Trap programs	91
2.6.6	Chromatographic conditions	92
2.7	Hatchery conditions	92
2.8	Parameters and samples analysis	93
2.9	Extraction of BPO enzyme from seaweeds	94

2.9.1	Enzyme crude extraction	95
2.9.2	Enzymatic assay	95
2.9.3	Protein test	96
2.10	References	100
3	Permanent site measurements	
3.1	Introduction	110
3.2	Study sites	111
3.3	Long-term air measurement sites	113
3.3.1	Tawau	113
3.3.2	Danum Valley	115
3.4	Result	117
3.4.1	Overview meteorological condition	118
3.4.2	Observations from the long-term measurement	125
3.4.2.1	Tawau site	125
3.4.2.2	Regression Analysis	130
3.4.2.3	Emission ratio	138
3.5	NAME model used for source emission prediction	149
3.6	Analyses and discussion	151
3.9	References	158
4	Cruise and campaign measurements	
4.1	Introduction	163
4.2	Ship-borne air measurement	167

4.3	June-August Malaysia halocarbons and Semporna campaign	170
4.4	Results and Discussion	173
4.4.1.1	<i>Perdana cruise</i> (PESC09) observation	173
4.4.1.1.1	Halocarbon measurements	173
4.4.1.2	Regional analysis	177
4.4.1.2.1	Straits of Malacca (Stations 1-3)	177
4.4.1.2.2	South China Sea (Stations 5 to 14)	177
4.4.1.2.3	Regional differences: Sulawesi and Sulu Seas (Stations 15-27)	178
4.4.1.3	Drivers of variability	179
4.4.1.3.1	Meteorological variability	180
4.4.1.3.2	Biological activity	182
4.4.1.4	Emission ratios	186
4.4.1.5	Total bromine	190
4.4.2	VLSL halocarbons campaign	191
4.4.2.1	Meteorological condition during Campaign	191
4.4.2.2	VLSL halocarbons measurements	194
4.4.2.2.1	Port Dickson (June 29 th to July 1 st , 2010)	194
4.4.2.2.2	Langkawi and Johor (August 5 th to 20 th , 2010)	200
4.4.2.2.3	Semporna seaweeds farm	201
4.4.2.2.4	Regression Analyses	204

4.4.3	Estimation of source emission	207
4.5	Conclusion	211
5	Determination of halocarbons in seawater and the the occurrence of BPO in marine seaweeds	
5.1	Introduction	225
5.2	Oceanic distribution of VSLs halocarbons	225
5.3	Seaweeds as a source of halocarbons?	227
5.3.1	Halocarbons production from marine algae	229
5.3.2	Previous studies on halocarbons productions	230
5.4	Mechanisms behind the productions	231
5.4.1	Natural occurring of halogenated compounds	231
5.4.2	The occurrence of haloperoxidase enzymatic activity in marine algae	233
5.4.2.1	Vanadium haloperoxidase	233
5.4.3	Purposed mechanisms of halocarbons from marine algae	
5.5	Seaweeds distributions at Malaysia	238
5.6	Objective of studies	243
5.7	Result and discussion	245
5.7.1	Seaweeds natural production experiment	245
5.7.1.1	The effect of seaweeds upon VSLs bromocarbons in seawater	245
5.7.2	Production rates of brominated compounds	251

5.7.3	Correlations of VSLs bromocarbons emissions and their implications	255
5.7.4	Influenced parameters on production rate	259
5.7.4.1	Surface seawater <i>Chl-a</i> and light intensity	259
5.7.3	The occurrence of BPO activity	264
5.8	Conclusion	267
5.9	References	268
6	General conclusions	
6.1	General conclusion	283
6.2	Future work	284
6.3	References	286
	Appendices	292

LIST OF FIGURES

Figure 1.1	Ozone concentrations in the stratosphere and troposphere	4
Figure 1.2	Common ozone abundances measurement techniques	5
Figure 1.2.1	Chapman theory reaction of ozone production and loss reaction	6
Figure 1.2.2	Catalytic ozone reactions in the stratosphere	7
Figure 1.2.3	Mechanism of ozone production in troposphere	9
Figure 1.2.4	Tropospheric ozone loss reactions	10
Figure 1.3	Radiative forcing of greenhouse gases contribution cause by anthropogenic activities in the atmosphere from 1975 to 2005	12
Figure 1.3.1	Ozone depletion or ‘Ozone hole’ at the Antarctic due to halogen monoxide	14
Figure 1.3.2	Tropospheric ozone loss reactions	15
Figure 1.4	Evaluation of selected ozone-depleting substances (ODSs) and substitute gases	18
Figure 1.4.1	The atmospheric abundances of individual ODSs at earth surface past and future prediction	22
Figure 1.5	Example of oceanic halocarbon production into the atmosphere	32
Figure 1.6	Halogen Source Gases Entering the Stratosphere in 2008	33
Figure 1.6.1	The dynamical pathways in the tropics transporting VSL source gases (SGs) and product gases (PGs) into the stratosphere	35
Figure 1.7	Summary activities in this study	45

Figure 2.1	Common volatile compounds extraction techniques used in environmental analysis	61
Figure 2.2	Simple setup for static headspace technique	64
Figure 2.2.1	Schematic diagram of the Purge and Trap system	66
Figure 2.3	The schematic diagram of μ -Dirac GC	71
Figure 2.3.1	The various stages of the GC method for a typical μ Dirac chromatogram	73
Figure 2.4	Stratum Tekmar Purge and Trap system diagram during purge and desorb steps.	83
Figure 2.5	Calibration linear regression curve for CHBr_3	87
Figure 2.5.1	Ion chromatogram for working standard of THM (4.94ngl^{-1}) in the seawater with purging time of 12 minutes	90
Figure 2.6	Incubation tub at Rimba Ilmu hatchery	94
Figure 2.7	Standard curve for protein determination using Lowry test	98
Figure 3.1	Ground based site at Kampung Batu Payung, Tawau	112
Figure 3.2	Kampung Batu Payung (KBP) observation lab at Tawau contained μ -Dirac	114
Figure 3.3(a)	The μ -Dirac GC located at KBP site	115
Figure 3.3(b)	Malaysian Meteorological Department (MMD) Global Atmospheric Watch (GAW) station in Danum Valley.	117

Figure 3.4	Schematic wind flow during South West Monsoon	119
Figure 3.4.1	Average <i>chl-a</i> concentration at measurement sites from October 2008 to April 2011	121
Figure 3.4.2(a)	The 10 days backtrajectories for 23 rd , 28 th November 2008 and 16 th December 2008 at KBP, Tawau	123
Figure 3.4.2(b)	The 10 days backtrajectories for 5 th February 2009 and 10 th November 2009 at KBP, Tawau	124
Figure 3.4.2.1(a)	Box plot for CHBr ₃ concentration from 2008 to 2011 (Tawau) and 2008 to 2009 (Danum).	127
Figure 3.4.2.1(b)	Box plot for CHBr ₃ concentration from 2008 to 2011 (Tawau) and 2008 to 2009 (Danum).	128
Figure 3.4.2.2	Linear plot CH ₂ Br ₂ against CHBr ₃ at KBP, Tawau for (a) whole months, coloured by month and b) to e) individual months.	135
Figure 3.4.2.3	CH ₂ Br ₂ /CHBr ₃ plotted against CHBr ₃ for a) all months, coloured by months and b) individual months.	140
Figure 3.5	Time series of VSLS bromocarbons mixing ratios during high event on selected days in a) November 2008, December 2008 and b) February 2009	142
Figure 3.6	Ratio of [CHBr ₃]/[CH ₂ Br ₂] versus the ratios of [CHBr ₂ Cl]/[CH ₂ Br ₂] for the selected months.	145
Figure 3.7.1	Selected days in December 2008 NAME air masses 10 days' backward trajectories at KBP, Tawau	154
Figure 3.7.2	Selected days in February 2009 NAME air masses 10 days' backward trajectories at KBP, Tawau.	155

Figure 3.7.3	Selected days in August 2009 NAME air masses 10 days' backward trajectories at KBP, Tawau	156
Figure 3.7.4	Selected days in December 2009 NAME air masses 10 days' backward trajectories at KBP, Tawau.	157
Figure 4.1	Sampling locations overlay with SeaWiFS <i>chl-a</i> during PESC 2009	169
Figure 4.2	VSLs halocarbons campaign measurements at Peninsular Malaysia (upper panel) and Semporna seaweeds farm, Sabah Borneo Malaysia (lower panel)	172
Figure 4.3	Bromocarbons and C ₂ Cl ₄ mixing ratios for each station during PESC 2009.	174
Figure 4.4	10 days air distribution backward trajectories calculated from the NOAA HYSPLIT model for each selected stations	182
Figure 4.4.1	<i>Chl-a</i> at the sampling stations from the CTD measurements against <i>chl-a</i> from satellite remote sensing	184
Figure 4.4.2	Halocarbon mixing ratios as a function of <i>in situ</i> measurements of <i>chl-a</i> in the water column	185
Figure 4.4.3	Correlations plot of CH ₂ Br ₂ and CHBr ₂ Cl versus CHBr ₃ mixing ratios	187
Figure 4.4.4(a)	Plot CH ₂ Br ₂ /CHBr ₃ and CHBr ₂ Cl/CHBr ₃ against CHBr ₃	189
Figure 4.4.4(b)	Log-log plots of CHBr ₃ /CH ₂ Br ₂ against CHBr ₂ Cl/CH ₂ Br ₂ for all stations during Perdana Cruise	189
Figure 4.5(a)	Sea Tides during campaign measurements at PD	193
Figure 4.5(b)	Sea Tides during campaign measurements at TB	193

Figure 4.5.1	Time series of VSLS bromocarbons at Ilham Resort, Cape Rachado PD	196
Figure 4.5.2	VSLS bromocarbons measured on 13 th January 2011 over seaweeds bed at Ilham resort, PD	198
Figure 4.5.3	Time series of VSLS chlorocarbons at Ilham Resort, Cape Rachado PD	199
Figure 4.5.4	Time series of VSLS halocarbons measurement during July-August 10	201
Figure 4.5.5	VSLS bromocarbons mixing ratios at different locations over <i>Kappaphycus</i> cultivation at Semporna seaweeds farm	203
Figure 4.6	Correlations between CH ₂ Br ₂ and CHBr ₂ Cl versus CHBr ₃ at Cape Rachado, PD	205
Figure 4.6.1	Correlations between CH ₂ Br ₂ and CHBr ₂ Cl versus CHBr ₃ at Tanjung Balau, Johor	206
Figure 4.6.2	Correlation between CH ₂ Br ₂ and CHBr ₂ Cl versus CHBr ₃ at Chenang Beach, Langkawi	206
Figure 4.6.3	Selected days in August 2010 NAME air masses 10 days' backward trajectories Chenang Beach, Langkawi	209
Figure 4.6.4	Selected days in August 2010 NAME air masses 10 days' backward trajectories Tanjung Balau, Johor	210
Figure 4.6.5	SeaWiFS chl-a concentration data during the campaign measurement	211
Figure 4.7.1(a)	Plot of CH ₂ Br ₂ /CHBr ₃ and CHBr ₂ Cl/CHBr ₃ against CHBr ₃	213

Figure 4.7.1b)	Log-log plots of $\text{CHBr}_3/\text{CH}_2\text{Br}_2$ against $\text{CHBr}_2\text{Cl}/\text{CH}_2\text{Br}_2$ for all stations during Perdana Cruise	213
Figure 4.7.2	Plot of $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ against CHBr_3 during PESC 09 and campaign	214
Figure 5.1	Natural halogenated compounds found in marine algae	233
Figure 5.2	The oxidation of halide by H_2O_2 which accomplish by BPO	
Figure 5.3	Scheme pathway of CHBr_3 production from green algae, <i>Penicillus capitatus</i> proposed by Beissner et al. (1981)	237
Figure 5.4	Scheme pathway of CHBr_3 production from green algae, <i>Penicillus capitatus</i> proposed by Morrison and Boyd (1992)	238
Figure 5.5	Sampling area for seaweeds collection at Cape Rachado, Port Dickson	240
Figure 5.5.1	Sampling area for seaweeds collection at Tanjung Balau, Desaru Johor	240
Figure 5.5.2	0.3mx0.3m quadrat used for estimation of seaweeds biomass	241
Figure 5.6	Ion chromatogram of samples (green seaweed) and blank (seawater).	247
Figure 5.6.1	Concentrations of VLS bromocarbons released in seawater from red seaweed	248
Figure 5.6.2	Concentrations of VLS bromocarbons released in seawater from brown seaweeds	249
Figure 5.6.3	Concentrations of VLS bromocarbons released in seawater from green seaweeds	250

Figure 5.6.4	Correlations of $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ (upper panel) and $\text{CHBr}_2\text{Cl}/\text{CHBr}_3$ (lower panel) measured in surface seawater contains 7 different types of seaweeds	257
Figure 5.6.5	In situ 24 hours average light intensity and <i>chl-a</i> during hatchery experiment	262

LIST OF TABLES

Table 1.1	Atmospheric lifetimes, global emissions, ozone depletion potential and global warming potentials of some halogen source and HFC substitute gases	17
Table 1.2	Lifetimes for very short-lived halogenated source gases	23
Table 1.3	Fluxes of bromine from bromoform (CHBr ₃) and dibromomethane (CH ₂ Br ₂) in Gg Br/yr, and iodine from methyl iodide (CH ₃ I) in Gg I/yr	26
Table 1.4	Summary of available observations of VSLS source gases from the marine boundary layer (MBL) to the tropical tropopause layer (TTL)	28
Table 2.1	μ -Dirac target compounds and measurement during Cape Verde ground-based and air craft campaign	69
Table 2.2	Limit of detection for THMs mixture in seawater	86
Table 2.3	Percentage mean recovery and relative standard deviation of each compound in seawater	90
Table 2.4	Preparation scheme using Lowry test	97
Table 3.1	Minimum, maximum and mean mixing ratios of CHBr ₃ and CH ₂ Br ₂ throughout the years at KBP, Tawau	129
Table 3.2	Linear regression correlation with respect to the CHBr ₃ for KBP, Tawau data set calculated for other VSLS bromocarbons, with slope m and correlation r^2	136
Table 4.1	Summary of measured VSLS halocarbons during PESC09	175

Table 4.2	Minimum, Maximum, Average and standard deviation of measured VSLS halocarbons at all sites	197
Table 5.1	List of seaweed species observed from December 2009 to March 2011 from Cape Rachado, Port Dickson	241
Table 5.2	Frequency and dominance (%) of seaweed species at Cape Rachado, Port Dickson from December 2009 to June 2010	242
Table 5.3	List of seaweed species for production rate experiment	243
Table 5.4	Minimum and maximum halocarbons concentrations in tub contain seawater for different types of seaweeds during 24 hours period.	251
Table 5.5	Production rate of naturally produced brominated compounds in 1000ml incubation bottles for different types of seaweeds.	254
Table 5.6	Total of Bromine release measured for seaweeds collected at the coastal of Port Dickson and Tanjung Balau.	254
Table 5.7	Correlations of well correlated compounds observed during hatchery tub experiment.	258
Table 5.8	Average VSLS bromocarbons ratios from hatchery tub experiment.	258
Table 5.6	Correlations between parameters influenced on the VSLS bromocarbons emission during hatchery experiment.	263
Table 5.7	Distribution of BPO activity in red, brown and green seaweeds from halocarbons production experiment.	267

LIST OF ABBREVIATIONS

BAS	British Antarctic Survey
BPO	bromoperoxidase
CFC	chlorofluorocarbon
CFC-115	chloropentafluoroethane (C ₂ ClF ₅)
<i>Chl-a</i>	chlorophyll <i>a</i>
HCFCs	hydrochlorofluorocarbons
CBL	convective boundary layer
CFC-114	dichlorotetrafluoroethane (ClF ₂ CCF ₂ Cl)
DOAS	differential optical absorption spectroscopy
ECD	electron captor detector
e.g.	for example
GC	gas chromatograph
GWPs	global warming potentials
<i>z</i>	height above sea surface [m]
LOD	Limit of detection
MBL	marine boundary layer
MS	mass spectroscopy
NOAA	National Oceanic and Atmospheric Administration (United States)
NEM	north east monsoon
N	north
NH	northern hemispheric
ODPs	Ozone depletion potentials
ODSs	Ozone depletion substances

OP3	oxidant and particle photochemical processes above a south-east Asian tropical rain forest project
PBL	planetary boundary layer
PGs	product gases
SST	sea surface temperature [°C]
sd	standard deviation
SGs	source gases
S	south
SWM	south west monsoon
SH	southern hemispheric
TBL	tropical boundary layer
VSLs	very short lived substances
VOCs	volatile organic compounds
W	west
WMO	World Meteorological Organization

LIST OF MOLECULAR FORMULAE

Br	bromine atom
BrO	bromine monoxide
CH ₂ BrCl	bromochloromethane
CHBr ₃	bromoform
CO ₂	carbon dioxide
CCl ₄	carbon tetrachloride
Cl	chlorine atom
ClO	chlorine monoxide
CF ₂ Cl	chlorodifluoromethane radical
CHCl ₃	chloroform
CHBr ₂ Cl	dibromochloromethane
CHBrCl ₂	dichlorobromomethane
CH ₂ Br ₂	dibromomethane
CF ₂ Cl ₂	dichlorodifluoromethane
HO ₂	hydrogen dioxide
H ₂ O ₂	hydrogen peroxidase
OH	hydroxyl radical
CH ₃ Cl	methyl chloride
NO ₂	nitrogen dioxide
NO	nitrogen oxide
O ₂	oxygen
O ₃	ozone
HO _x	term for HO or HO ₂
NO _x	term for NO or NO ₂
C ₂ Cl ₄	Tetrachloroethelyne

CFC-11

trichlorofluoromethane (CCl_3F)

CFC-113

trichlorotrifluoroethane ($\text{CCl}_2\text{FCClF}_2$)

LIST OF SYMBOLS

atm	atmosphere (as pressure unit)
τ	atmospheric lifetimes
$O^1(D)$	atom yield from photolysis of ozone
p	barometric pressure [mbar or hPa]
'	minute (unit for positions)
%	percent
P	production rate per unit volume
t	time
<i>uv</i>	ultraviolet radiation

LIST OF UNITS

cm	centimetre (10^{-2} metres)
cm ³	centimetre cube
d	day (as time unit)
°C	degree Celsius
Gg	gigagram (10^9 grams)
Gmol	gigamole (10^9 moles)
hPa	hecto pascal (10^2 pascal)
hr	hour (as time unit)
“	inch
K	kelvin
Km	Kilometre
Kpa	kilopascal (10^3 pascal)
L	litre
Mmol	megamole (10^6 moles)
m	metre
µg	microgram (10^{-6} grams)
mbar	millibar (10^{-3} bars)
mg	milligram (10^{-3} grams)
ml	millilitre (10^{-3} litres)
mm	millimetre (10^{-3} metres)
mmol	millimole (10^{-3} moles)
m	minute (as time unit)
Mol	mole
ng	nanogram (10^{-9} grams)
nm	nanometre (10^{-9} metres)

nmol	nanomole (10^{-9} moles)
pmol	picomole (10^{-12} moles)
Pa	pascal (pressure unit)
ppb	part per billion
ppm	part per million
ppt	part per trillion
patm	picoatmospheres (10^{-12} atmospheres, or 1.01325×10^{-7} Pa)
pmol	picomole (10^{-12} moles)
s	second (as time unit)
kelvin	temperature [K]
yr	year (as time unit)