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 tetrechloroethylene (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 dilengkapkan 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 rumpai laut, dan tidak melalui penghasilan biologi terus oleh fitoplankton atau bacteria. Eksperimen telah dilakukan ke atas 7 jenis rumpai 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 eskperimen 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 g^{-1} FW^{-1} h^{-1}, di mana rumpai laut merah merupakan pengeluar tertinggi, diukuti oleh rumpai laut coklat dan hijau. Enzim bromoperoksidase (BPO) juga telah diekstrak daripada semua jenis rumpai laut, dan keputusan menunjukkan keaktifan BPO yang tinggi bagi rumpai 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.

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LIST OF ABBREVIATIONS

BAS	British Antarctic Survey
BPO	bromoperoxidase
CFC	chlorofluorocarbon
CFC-115	chloropentafluoroethane (C_2ClF_5)
Chl-a	chlorophyll *a*
HCFCs	hydrochlorofluorocarbons
CBL	convective boundary layer
CFC-114	dichlorotetrafluoroethane (ClF_2CCF_2Cl)
DOAS	differential optical absorption spectroscopy
ECD	electron captor detector
e.g.	for example
GC	gas chromatograph
GWPs	global warming potentials
z	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_2BrCl	bromochloromethane
$CHBr_3$	bromoform
CO_2	carbon dioxide
CCl_4	carbon tetrachloride
Cl	chlorine atom
ClO	chlorine monoxide
CF_2Cl	chlorodifluoromethane radical
$CHCl_3$	chloroform
$CHBr_2Cl$	dibromochloromethane
$CHBrCl_2$	dichlorobromomethane
CH_2Br_2	dibromomethane
CF_2Cl_2	dichlorodifluoromethane
HO_2	hydrogen dioxide
H_2O_2	hydrogen peroxidase
OH	hydroxyl radical
CH_3Cl	methyl chloride
NO_2	nitrogen dioxide
NO	nitrogen oxide
O_2	oxygen
O_3	ozone
HOx	term for HO or HO_2
NOx	term for NO or NO_2
C_2Cl_4	Tetrachloroethelyne

CFC-11	trichloroflouromethane (CCl_3F)
CFC-113	trichlorotrifluoroethane (CCl_2FCClF_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
uv	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)