Bromocarbons over the Coastal Area in Peninsular Malaysia

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Abstract. Concentration of bromoform (CHBr₃), dibromochloromethane (CHBr₂Cl) and dichlorobromomethane (CHBrCl₂) in seawater was analysed to determine the concentrations at Cape Rachado, Negeri Sembilan (mangrove area) and Melawi Beach, Kelantan (coastal area) and factors that can influenced the concentrations. Seawater samples have been identified and quantify by using purge-and-trap concentrator (P&T) and gas chromatography equipped with electron captured detector (GC/ECD). Mean value of CHBr₃ at Cape Rachado is 0.010 mmol/L and Melawi Beach is 0.001 mmol/L. The major brominated halocarbons at Cape Rachado and Melawi Beach is CHBr₃ with range value 0.009 – 0.012 mmol/L and 0.0004 – 0.0021 mmol/L, respectively. Concentrations of CHBr₃, CHBr₂Cl and CHBrCl₂ at Cape Rachado (mangrove area) are higher than Melawi Beach (coastal area) because the located at seaweed bed and adjacent to mangrove swamp.

1. Introduction
Emissions of biogenic halocarbons showed large variability and mainly based on natural oceanic origin, especially in tropical coastal such as salt marshes and mangrove that locates large diversity of phytoplankton and macroalgae [1][2]. Study on bromocarbons from tropical latitudes ocean critically important because of deep convection allows for a rapid ascent of the bromine compounds from the marine boundary layer to tropical tropospheric layer (TTL). Also, transport pathways from marine boundary layer to the TTL are important to identify for assessing stratospheric ozone depletion [3]. Emphasis on bromocarbons study is because as they are readily oxidised and formed highly ozone-depleting inorganic bromine compounds [4].

The goal of this study is to determine the concentration of bromocarbons (CHBr₃, CHBr₂Cl and CHBrCl₂) at different areas (coastal and mangrove area) by using purge-and-trap concentrator (P&T) and gas chromatography with electron captured detector (GC/ECD) and identify the factors that contribute to the presence.
2. Methodology

2.1 Study site

Water samples were collected from Cape Rachado, Negeri Sembilan (area A) and Eastern Coast, Melawi Beach, Bachok, Kelantan (area B) during North-East Monsoon (November to March). Both areas have two monsoon seasons, north-east and south-west with mean annual rainfall about 2,500 mm, range of temperature is from 25°C to 32°C and wind flow 10 to 20 knots.

Cape Rachado (2°24’54.63” N, 101°51’16.21” E) is located in the south-western region of the state of Negeri Sembilan, Malaysia, facing Straits of Malacca and approximately about 18 km south from Port Dickson town. This nature attraction becomes favourite spot for bird watching during migratory season of raptors, also have hidden beaches, mangrove swamp and famous picnic area. Area A has a fringing coral reef flats extend out about 50 m, gently slope off about 8 m towards the reef edge [5]. The reef flats were completely exposed when the tidal level is about less than 0.1 m from chart datum [6].

Melawi Beach (6°0’33.77” N, 102°25’37.64” E) is located 37 km south from Kota Bharu town, capital of Kelantan or approximately 45 min driving by car and facing South China Sea (SCS). Famous location among tourists and local peoples because it located away from the bustling town and many accommodations was built near Melawi Beach. Other than that, Melawi Beach is adjacent to a small port for fishing, Tok Bali which has served as jumped-off point for tourists to go to Perhentian Islands. Sampling locations are shown in Figure 1.

2.2 Sampling technique

Collections of water sample were taken from each area according to standard methodologies, during daylight and low tidal level with maximum level of 0.8 m. Niskin sampler 4 L (OSIL, UK) was used to collect the samples and placed in Schott bottle wrapped with aluminum foil without headspace. Collected samples were stored in lightproof insulated box with ice pack and water for rapid cooling before being transported back and stored in chest freezer in laboratory at 4°C for less than one week to prior to analysis. Location was located by GPS and in-situ parameters (water temperature, pH and dissolved oxygen) readings were taken by portable YSI Multi-probe field meter model 556. Replicate of samples not less than three. The study conducted is short term measurement. Sampling details are shown in Table 1.
Figure 1. Map of study areas: (a) Cape Rachado and (b) Melawi Beach.

Table 1. Descriptions of at Cape Rachado and Melawi Beach.

| Study area               | Coordinate          | Description                                                                 |
|--------------------------|---------------------|-----------------------------------------------------------------------------|
| Cape Rachado (area A)    | 2° 24’ 54.63” N    | Mangrove swamp, forest, coral reef, seaweed bed, recreation and vacations areas. |
|                          | 101° 51’ 16.21” E  |                                                                             |
| Melawi Beach (area B)    | 6° 0’ 33.77” N     | Fishing, recreation and vacation areas.                                     |
|                          | 102° 25’ 37.64” E  |                                                                             |
2.3 Instrumentation and analysis

For calibration, a stock solution of a Trihalomethane mixture (Sigma, US) containing each compound at 200 mg/L in methanol were diluted to 5 different concentrations in pure methanol (Merck, Germany) placed in amber bottle and stored at 4ºC for less than one week. The internal standard solution consists four compounds, CHBr3, CHCl3, CHBr2Cl and CHBrCl2 but this study focused to bromocarbons only. Calibration were performed by spiked a few mg/L of mixed standard solution into a system, from low to high concentrations and followed by sample analysis. Each concentration of standard solution and sample was analyzed not less than three times (triplicates). The peak areas for each quantify ions were recorded against known concentration bromocarbons and fitted into linear equation derived to determine the concentrations of compounds.

Bromocarbons analysis was performed with Tekmar Dohrmann 3100 purge-and-trap concentrator (Tekmar, Ohio) coupled with Varian CP-3800 Gas Chromatograph - Electron Captured Detector (Varian,USA). The instrument was controlled and interpreted chromatograph data by GC Workstation Version 6.41 software. A 5 mL filtered water sample was manually injected into purge-and-trap system, purged with pure nitrogen (N2) gas to extract the volatile compounds at a flow-rate 40 mL/min for 11 min ± 0.1 min at ambient temperature. The extracted & trapped gases moved to desorption stage at temperature of 180ºC for 4 min before transfer to GC/ECD for identification and quantification phase.

Identification and quantification of compounds were performed with fitted narrow-bore DB5 column (J&W, USA), 30 m length, 0.32 mm internal diameter and 1.0 µm film thickness. Detector used nitrogen (N2) as make-up gas at 60 mL/min and high purity helium (He) as carrier gas at 2.5 mL/min. GC/ECD was set to temperature program: 40 ºC for 5 min, 130 ºC at 8 ºC/min, 180ºC at 25ºC/min and held for 5 min for last temperature. The temperature of column, injector and detector was controlled at 40 ºC, 200 ºC and 250 ºC respectively. Total time for analysis samples with P&T and GC/ECD is 41 min.

3 Result and Discussion

The method optimised for detection of bromocarbons (CHBr3, CHBr2Cl and CHBrCl2) in seawater samples from mangrove and coastal areas. The limit of detection (LOD) for each bromocarbon compound by using GC/ECD are 0.3 fmol/L for CHBr3, 0.2 fmol/L for CHBr2Cl and 0.4 fmol/L for CHBrCl2. Retention time for CHBr3 is 9.254 min, CHBr2Cl is 6.637 min and 4.143 min for CHBrCl2. Recoveries obtained for CHBr3 is 84.7 – 89.4%, CHBr2Cl is 81.5 – 86.6% while CHBrCl2 is 79.4 – 80.7%. The mean value of seawater quality for in-situ parameters are 28.1 – 33.5ºC for seawater temperature, 8.71 – 10.50 mg/L for dissolved oxygen and 8.21 – 8.71 for pH.

Result of bromocarbons in seawater samples obtained from sampling at two different areas, mangrove and coastal are showed in Figures (a) and (b), respectively. Range concentrations for each compound from mangrove area are 0.009 – 0.012 mmol/L for CHBr3, 0.005 – 0.006 mmol/L for CHBr2Cl and 0.006 – 0.008 mmol/L for CHBrCl2. Mean value of CHBr3 is 0.010 mmol/L, highest than mean value of CHBr2Cl (0.006 mmol/L) and CHBrCl2 (0.007 mmol/L). A presence of bromocarbon compounds in seawater is because the study area is located at seaweed bed and adjacent to small patch of mangrove. Seaweeds or macroalgae functional as collector that collects halides from seawater uptakes and produce halocarbons by oxidation process [7]. From observation, geographical condition at study area has abundance of lime stones and rocks at sea ground are suitable for macroalgae to develop and growth [8]. Cape Rachado dominated by the brown seaweed (Sargassum binderi, Turbinaria comoides and Padina australis), followed by green and red seaweed. Brown algae known as major contributor of brominated halocarbons compared with green and red algae [9].
Concentration of CHBr$_3$ in seawater from coastal area still dominated compared with another two compounds, CHBr$_2$Cl and CHBrCl$_2$. Concentrations range value for bromocarbons from coastal area are 0.0004 – 0.0021 mmol/L for CHBr$_3$, 0.0007 – 0.0012 mmol/L for CHBr$_2$Cl while for CHBrCl$_2$ is 0.0003 - 0.0004 mmol/L. Mean value of CHBrCl$_2$ (0.0003 mmol/L) is the lowest compared to CHBr$_3$ and CHBr$_2$Cl. Concentration of CHBr$_3$ increased when phytoplankton increased [10]. Based on observation along coastline at Melawi Beach, there is no presence of seaweed bed. Thus, concentrations of bromocarbons at Melawi Beach may not be influenced by seaweed emissions. Detected bromocarbons in seawater could be contributing by microalgae such as phytoplankton [11]. Another factor that could be the influence the bromocarbons concentration is wind direction. Movement of atmospheric bromocarbons can be explained with software NOAA Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model by using 3 days backward trajectory to indicate the transportation of air masses to study area. Figure 3 showed the transportation of air masses during sampling time. The air masses transports from Northeast Peninsular Malaysia bring together the emissions from South China Sea (SCS) before arrived to Melawi Beach. Emissions from SCS and phytoplankton can be the factors in influenced bromocarbons concentrations.
FIGURE 2. (a) Concentrations of bromocarbons in seawater from mangrove area. (b) Concentrations of bromocarbons in seawater from coastal area.

Figure 3. Transportation of air mass by NOAA HYSPLIT 3 days backward trajectories to Melawi Beach.

4. Conclusion

It was concluded that CHBr$_3$ was the dominant bromocarbons at mangrove and coastal area compared to CHBr$_2$Cl and CHBrCl$_2$. The analysis showed, seaweed and mangrove trees are the sources of CHBr$_3$, CHBr$_2$Cl and CHBrCl$_2$ in seawater at Cape Rachado, while phytoplankton and air masses from North East Peninsula through South China Sea (SCS) can be sources of bromocarbons at Melawi Beach. Mean value of CHBr$_3$ at Cape Rachado (0.010 mmol/L) is higher than Melawi Beach (0.001 mmol/L). Also, range value for concentrations of bromocarbons at Cape Rachado higher than Melawi Beach with 0.009 – 0.012 mmol/L for CHBr$_3$, 0.005 – 0.006 mmol/L for CHBr$_2$Cl and 0.006 – 0.008 mmol/L for CHBrCl$_2$.

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