

## **Short-term variability in halocarbons in relation to phytoplankton pigments in coastal waters of the central eastern Arabian Sea**

Rajdeep Roy

Chemical Oceanography Division, National Institute of Oceanography, CSIR,  
Dona Paula, Goa, India. 403004.

**Phone:** +91-832-2450403/2451159

**Fax:** +91-832-2450607

**Email:** [rajdeeproy2003@yahoo.com](mailto:rajdeeproy2003@yahoo.com)

---

### **Abstract**

Halocarbons released from oceans are known to be important in atmospheric processes. Their abundance in seawater is influenced by water column conditions and phytoplankton community. In the present attempt, halocarbon abundances together with pigment composition were monitored in the coastal waters of the central eastern Arabian Sea. Short-term variability for the period April 2005 to March 2007 was studied for chlorinated hydrocarbons ( $\text{CHCl}_3$ ,  $\text{CCl}_4$ ) and bromocarbons ( $\text{CH}_2\text{Br}_2$  and  $\text{CHBr}_3$ ) for the first time in the Arabian Sea. Variability in pigments was used to understand the influence of phytoplankton community composition on halocarbon concentrations in this region. Halocarbons and phytoplankton pigments showed strong short-term variability, with maximal values generally associated with southwest (summer) monsoon high productivity. Decreased chlorocarbon abundances in subsurface layers indicate their possible consumption under oxygen deficient conditions, particularly during the summer monsoon and fall-intermonsoon periods. Halocarbon abundances were in the order  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$  and  $\text{CCl}_4$ . The  $\text{CHCl}_3$  showed significant positive relationship with fucoxanthin ( $r = 0.93$ ,  $p = 0.001$ ,  $n = 155$ ) suggesting the importance of diatoms and prymnesiophytes in the Arabian Sea. Among the phytoplankton pigments Chlorophyll-*a* showed positive relationship with marker pigment fucoxanthin. Of the four phytoplankton groups studied the percent dominance was in the order: diatoms > nanoflagellates > cyanobacteria > dinoflagellates. Our study shows utilization of halocarbons during microbial oxidation of organic matter could be a significant sink of these compounds although they might be produced in significant quantities by biochemical processes during high productivity periods, as can be seen from our observations in summer monsoon in the Arabian Sea.

**Key words:** Chlorinated hydrocarbons; Community composition; Phytoplankton; Diatoms; Pigments; Arabian Sea;

---

## 1. Introduction

Halocarbons of marine origin are significant sources of reactive halogen species in the troposphere (Lovelock et al., 1975; Rasmussen et al., 1982). The marine biogenic sources are phytoplankton (Singh et al., 1983; Tokarczyk and Moore, 1994; Tait and Moore 1995; Moore et al., 1996; Scarratt and Moore, 1998) and macro algae (Ekdahl et al., 1998; Manley et al., 1992). Enzymatic reactions involving haloperoxidase have been found to be primarily responsible for the production of halocarbon compounds in both micro and macroalgae (Scarratt and Moore, 1996; Wever et al., 1991). For example, bromoperoxidase enzymes lead to the production of brominated halocarbons (Abrahamsson et al., 2003). The production of halocarbons is believed to help in countering the oxidative stress (Mtolera et al., 1996) and grazing. The extent of production of halocarbon compounds have been shown to be phytoplankton species dependent (Tokarczyk and Moore, 1994). Photochemical formation assumes near equal importance for some compounds, such as iodinated carbons in the open ocean (Bell et al., 2002; Happell and Wallace, 1996; Moore and Zafiriou, 1994; Richter and Wallace, 2004; Yokouchi et al., 2001). Loss of halocarbons in the water column potentially occurs through halide substitution, hydrolysis (Elliot and Rowland, 1995), photolysis (Zafiriou et al., 1974) and biological (King and Saltzman 1997, Goodwin et al., 1997) processes.

The bromocarbon compounds have been measured extensively than chlorocarbons (see review by Quack and Wallace, 2003; Carpenter et al, 2007; Quack et al., 2007) in view of their importance in atmospheric reactions. The  $\text{CHBr}_3$  is an established source of bromine atoms in the upper troposphere (Yang et al., 2005; Salawitch, 2006) although inherent mechanisms involved are poorly understood. Elevated concentrations of dibromomethane ( $\text{CH}_2\text{Br}_2$ ) and bromoform ( $\text{CHBr}_3$ ) in the open ocean have often been linked to marine phytoplankton (Baker et al., 2000; Klick and Abrahamsson, 1992; Class and Ballschmiter, 1988; Quack and Wallace, 2003; Quack et al., 2007). The  $\text{CCl}_4$  presence has been attributed to anthropogenic activities, which has been found in coastal and open ocean regions (Fogelqvist, 1985; 74 and ref there in), and Antarctic glaciers (Zoccolillo et al., 2004) indicating its wide spread occurrence, As the it has predominant external source  $\text{CCl}_4$  is being potentially used to trace water masses in the ocean (Krysell, 1992; Tanhua and Olsson, 2005), although its loss due to reduction in anoxic environment is noted (Krysell et al; 1994).

The Arabian Sea is the most biologically productive region in the Indian Ocean; the maximal of it occurring in the southwest (summer or SWM) monsoon. The summer monsoon winds result in the western boundary upwelling off Somalia and Arabia whereas the west coast of India experiences minor upwelling. In the northeast (winter or NEM) monsoon the productivity is largely supported by convection in the Arabian Sea. The circulation along the coast of India is also associated with summer and winter monsoons (Shetye, 1998). Occurrence of coastal hypoxia along the west coast of India has been found (Naqvi et al., 2000) which is of biogeochemical and environmental importance. Significant emissions of dissolved gases of climate relevance have been reported from the Arabian Sea (Naqvi et al., 2000; Sarma et al., 1998; Bange et al., 1998; Patra et al., 1998; Upstill-Goddard et al., 1999; Jayakumar et al., 2001; Shenoy and Kumar, 2007) however no information is available on biogenic halocarbons abundances and their distributions in this biogeochemically and climatically important monsoon region.

Therefore, in the present attempt we studied the short-term variability in four halogenated compounds in the coastal Arabian Sea off Goa (central west coast of India) with reference to changes in phytoplankton communities (as derived from pigments) and the occurrence of seasonal hypoxia.

## **2. Material and methods**

### *2.1. Sampling*

The sampling locations, along the Candolim Time-Series Section (CaTS), in coastal waters of the eastern Arabian Sea, are shown in Fig. 1. Water depth at these stations varied between 6 m (G1) and 28 m (G5) whereas samples at G5 were generally collected from a fixed depth of 1m, 9m, 18m and 25m. Field observations were made at monthly intervals, particularly at G5 but variable at other stations, between April 2005 and April 2007 using fishing trawlers. Vertical profiles of temperature, salinity and oxygen were taken using portable Conductivity-Temperature-Depth (CTD) System (Sea Logger, Sea Bird, SBE 25). Water samples were collected using Niskin bottles of 5 litre capacity fixed to a nylon rope. During the study period, pigment samples were collected 25 times between (April 2005-March 2007), chlorocarbons from December 2005 to April 2007 and bromocarbons between August 2006 and April 2007. Due to logistic reasons (mainly due to restriction of Captain of Ports for using fishing trawlers and the non-availability of a suitable bigger vessel) the sampling could not be regular during the most turbulent monsoon season. Nevertheless, efforts were made to cover particularly the latter part (August-September) of the SWM period (June–September), Fall Intermonsoon (FIM) period (October-

December), NEM (December-February), and Spring Intermonsoon (SIM, March-May) the section was covered at least once a month.

Water samples for halogenated compounds were drawn (immediately after oxygen sampling) gently into 100 ml volumetric flasks and allowed approximately 200 ml of water sample to over flow. The flasks were then closed using glass stopper, immediately kept in dark at 4°C and stored until analysis. For the pigment analysis, 1-2 liters of water sample was immediately filtered using a GF/F filter (pore size 0.7 µm) avoiding exposure to direct light and high temperature. The filter paper was stored in liquid nitrogen until analysis in the shore laboratory.

(Fig. 1)

## 2.2 Pigments analysis

Phytoplankton Pigments from the frozen filters were extracted into 3 ml 95% acetone (v/v in deionized water) in 5 minutes, under low light and temperature (4°C) conditions, using ultrasonic bath (5 sec, 20 kHz) filled with ice-water. The extracts were stored overnight at -20°C for high performance liquid chromatography (HPLC) analysis. The extract was passed through a Teflon syringe cartridge (Millipore) having a glass fiber pre acrodisc filter (pore size 0.45 µm, diameter 25 mm) to remove the cellular debris. The clear extract was collected in a 5 ml glass vial and placed directly into the temperature controlled (5°C) auto-sampler tray for HPLC analysis. Entire extraction procedure was carried out in dim light conditions and at low temperature to minimize degradation of pigments. The HPLC analysis was carried out following the method of Van Heukelem, (2002) as detailed in Roy et al., (2006). In the present attempt, the sum of 19'-hexanoyloxyfucoxanthin (19'HF), 19'-butanoyloxyfucoxanthin (19'BF), Alloxanthin (Allo) and Chlorophyll b was used to indicate nanoflagellates abundance. Zeaxanthin (Zea), fucoxanthin (Fuc) and peridinin (Per) were considered to represent cyanobacteria, diatoms and dinoflagellates, respectively. Diagnostic pigment (DP) indices were calculated following the method of Barlow et al. (2007) for assessing the phytoplankton communities. DPIs were derived from biomarker pigments as per details given in Table 1. Four major groups were evaluated. The indices symbolizing the groups were designated as Diat<sub>DP</sub> (diatoms); Dino<sub>DP</sub> (dinoflagellates); Flag<sub>DP</sub> (nanoflagellates); Prok<sub>DP</sub> (Prokaryotes) and proportion of each group contributing to the biomass was defined as given in Table 1.

(Table 1)

### 2.3. Halocarbons analysis

Halocarbons extraction was performed by following the procedure of (Abrahamsson and Klick, 1990), which is widely used in view of its lower detection limits and simplicity (Fogelqvist, 1985; Laternus et al., 1996; Russo et al., 2003; Zoccolillo et al., 2004). Distilled pentane (2 ml) from Sigma Aldrich was added directly into the cold water samples. The flasks were shaken vigorously for 5 min and then kept at 4°C for 30 min to allow separation of the organic phase. The whole extraction was done under dim light conditions and in a cool environment to prevent photo-dissociation of halocarbons and minimize the loss of solvent. A Varian gas chromatograph (model CP3800) with megabore column was used. The electron capture detector (ECD) detector was maintained at 290°C with nitrogen as the make up and helium as carrier gases with a flow rates of 30 and 5 ml min<sup>-1</sup>, respectively. Column temperature was maintained initially at 40°C for 1 min and then raised, at a rate of 4°C min<sup>-1</sup>, with a final hold at 180°C for 25 min, for removing the non-volatile impurities. Two mega bore columns DB 624 (60 m, ID 0.53 mm, film thickness 3 µm) and HP5 (15 m, ID 0.53 mm, film thickness 1.50 µm) of different polarities were joined with fused silica connector (Supelco, Germany) to achieve better separation. A 3 µl sample extract was directly injected into the column at an injector temperature of 90°C. By this method the base line separation was found to be very good. Identification of sample peaks was based on retention times, as confirmed by routine spiking of respective standards. Detection limits, defined as signal (S) to noise (N) ratio (S/N=5), were determined by spiking seawater samples with the halogen compounds being analyzed. The precisions were expressed as relative standard deviations of quadruplicate analyses of spiked seawater samples. The precisions were found to be in the range of 7.2-9.7% whereas the detection limits were between 0.01 and 1.2 ng l<sup>-1</sup>, for the four halocarbons studied. Calibration was achieved with a four point external standard calibration procedure (ESTD), using individual synthetic standards obtained from Sigma Aldrich, (Germany). The calibration curve for each compound was prepared by running different dilutions of the synthetic standards in methanol (Chromasolv) and the respective peak areas. As a routine experiment one mixed standard was then run daily along with samples to check the calibrations and, if any, variations in retention times.

### 3. Results

The short-term variability of halocarbons and pigments has been presented for CaTS station G5, with a brief on hydrography. However, data from stations G1- G4 have been used to derive statistically significant relationships among the halocarbons and phytoplankton pigments.

#### 3.1 Hydrographic conditions

During March (SIM), the temperature of the water column at CaTS station G5 was between 28.1 and 28.8 whereas oxygen concentrations were within 108-195  $\mu\text{M}$ . Temperature was low (23.2-24.6  $^{\circ}\text{C}$ ) with maximal change in oxygen (0-207  $\mu\text{M}$ ) in the water column during August (SWM) due to intense upwelling. The water column temperature in October (FIM) ranged between 27.1 and 29.1  $^{\circ}\text{C}$ . Dissolved oxygen showed a strong vertical gradient varying within 55-208  $\mu\text{M}$ . Even though bottom waters were not anoxic during October the oxygen concentration still remained relatively low. The water column was well mixed in January (NEM) with a relatively uniform temperature of 28.3-28.7 $^{\circ}\text{C}$  while oxygen concentration varied between 127 and 260  $\mu\text{M}$ .

#### 3.2. Variability of phytoplankton pigments

Changes in phytoplankton pigments are depicted in Fig. 2. The most abundant pigment, chlorophyll-*a*, at station G5 occurred at a mean value of 111  $\text{ng l}^{-1}$  (range of 10-595  $\text{ng l}^{-1}$ ). Higher concentrations of chlorophyll *a* were generally recorded during the SWM while extremely lower values were found in the SIM period. Fucoxanthin was the next most abundant pigment found that had a mean value of 14  $\text{ng l}^{-1}$  (range: 3-50  $\text{ng l}^{-1}$ ). Marked increase in fucoxanthin was generally observed during the SWM (mainly August-September) presumably due to increased growth of diatoms and prymnesiophytes. Zeaxanthin, the marker pigment of cyanobacteria, also exhibited strong variability in the range of 1-29  $\text{ng l}^{-1}$  (mean concentration of 6  $\text{ng l}^{-1}$ ). Peridinin concentration varied in the range of 1-15  $\text{ng l}^{-1}$  (mean = 3  $\text{ng l}^{-1}$ ). The nanoflagellates pigment composition was dominated by prymnesiophytes and green algae, the total of which varied between 3 and 16  $\text{ng l}^{-1}$  and was higher during the FIM season.

(Fig.2 and Fig. 3)

### 3.3 Variability in halocarbons

The  $\text{CHCl}_3$  at G5 occurred at a mean concentration of  $38.9 \text{ ng l}^{-1}$  (range :  $<0.01\text{-}197.5 \text{ ng l}^{-1}$ ). Higher concentrations of  $\text{CHCl}_3$ , in the water column, were found between September and January with maximal values towards the end of the SWM (Fig. 3). Very high value also occurred at the bottom of March 2006 but not recurred in March 2007. The higher concentrations in September 2006 were found closer to the surface. The  $\text{CCl}_4$  occurred at a mean concentration of  $0.9 \text{ ng l}^{-1}$  (with a range of  $0.01\text{-}3.69 \text{ ng l}^{-1}$ ). Maximal concentration of  $3.69$  occurred in August (SWM) in the upper water column.

Two brominated compounds studied showed higher concentrations and exhibited strong association with SWM processes (Fig. 3). The mean concentration of  $\text{CH}_2\text{Br}_2$  was relatively higher ( $39.3 \text{ ng l}^{-1}$ ; range =  $<1.2\text{-}156.4 \text{ ng l}^{-1}$ ) than that of  $\text{CHBr}_3$  ( $20.5 \text{ ng l}^{-1}$ ; range =  $<0.3\text{-}265.4 \text{ ng l}^{-1}$ ). The  $\text{CH}_2\text{Br}_2$  also exhibited another peak, which almost equaled that in SWM, in January (NEM). It is interesting to note that the concentrations of these two brominated compounds remained high from SWM to NEM (August to January) with minimal levels in SIM season.

(Fig. 4)

## 4.0 Discussion

### 4.1 Hydrography

The Arabian Sea circulation is strongly influenced by summer and winter monsoons with reversals in coastal currents (Shetye, 1998; Shankar et al., 2002). During the SWM the surface flow is directed towards the equator while the subsurface current moves in the opposite direction. The equatorward surface flow is accompanied by upwelling, as in other eastern boundary environments, which begins off the southwest coast of India and the west coast of Sri Lanka around May. Upwelling propagates northward upto November-December reaching Mumbai coastal region even after the collapse of the SWM winds. The influence of seasonal circulation is well reflected in the presently observed temperature and oxygen distributions. Upwelling together with intense freshwater discharge from land in SWM creates strong surface stratification in the study region. Upwelling (with low temperatures of  $23.2\text{-}24.6^\circ\text{C}$ ) induced intense biological productivity (Fig. 2) and the stratification results in oxygen depleted conditions in the subsurface layers that caused strong gradient of  $0\text{-}207 \mu\text{M}$  in August. The influence of upwelling and stratification, although decreased to some extent, continued till

October as can be seen in water column conditions when oxygen ( $55 \mu\text{M}$ ) was much below saturation. However, during NEM and SIM seasons the coastal water column off Goa is well mixed with minimal gradients in temperature and oxygen. The observed hydrographic features are in good agreement with evolution of oxygen deficient conditions along the west coast of India (Naqvi et al., 2006a).

#### *4.2 Variability in pigments and phytoplankton composition*

Upwelling and convection along the west coast of India are important as these processes promote biological productivity. Thus productivity of phyto-and zooplankton and their abundance in the water column show clear seasonality (Sawant and Madhupratap, 1996; Gauns et al., 1996; Ramaiah et al., 1996). Maximal production ( $1782 \text{ mg C m}^{-2} \text{ d}^{-1}$ ) in the eastern Arabian Sea is found to occur during the south west monsoon (Prasannakumar et al., 2001). A significant biogeochemical process of the study region is the occurrence of coastal hypoxia along the west coast of India (Naqvi et al., 2000; 2006a). Seasonal occurrence of coastal hypoxia has been found to be facilitated by the spread of a low salinity stratified layer (of about 2 m thick) over the upwelled waters that are already low in oxygen. Thus the short-term variability in hydrographic characteristic of this region shows strong build up of oxygen deficient environment during and after the southwest monsoon (Naqvi et al., 2006a). Below this low salinity cap, upwelling water is indicated by nutrient rich but sensitive redox environment. Upwelled waters that are already low in oxygen are further burdened by higher organic loading following the enhanced productivity in summer monsoon, as indicated by higher chlorophyll *a* and fucoxanthin abundances (Fig. 2), that results in hypoxic to anoxic conditions.

The distribution of accessory pigments provides information on the dominant phytoplankton communities. Different marker pigments related to individual groups were grouped together based on notation reported earlier (Vidussi et al., 2001; Barlow et al., 2005; Barlow et al., 2007). Coastal upwelling during the SWM brings nutrient rich subsurface waters to the euphotic zone resulting in increase in the biomass of larger cells including both diatoms and dinoflagellates. This is supported by significant increases in fucoxanthin and peridinin during this season (Figs. 2). As upwelled nitrate is consumed diatoms and dinoflagellates dominance decrease while the contribution of small green flagellates and cyanobacteria increase (Fig. 2, 3). Marked vertical changes in pigment levels are also seen at G5. At surface diatoms (fucoxanthin) reached the diagnostic index of 0.8 in SWM of 2005 but in the following SWM it was  $\sim 0.4$  (Fig. 3). On an annual basis (G5), of the four major plankton groups



(diatoms, nanoflagellates, cyanobacteria and dinoflagellates) studied, diatom contribution increased from 43% (at surface) to 56% (bottom) at the expense of nanoflagellates and cyanobacteria. Dinoflagellates contributions remained vertically invariant. Of the four groups the percent dominance at G5 is in the order: diatoms > nanoflagellates > cyanobacteria > dinoflagellates. From the results it appears that during premonsoon the cyanobacteria becomes significant whereas in monsoon the study area is dominated by the larger cells (diatoms and dinoflagellates). In the post monsoon small nanoflagellates were more important. Our results broadly agree with those that suggest seasonal variations in winds cause marked changes in phytoplankton composition in the Arabian Sea (Latasa and Bidagare, 1998; Barlow et al., 1999, Parab et al., 2006).

Statistical analysis of pigment data (Fig. 5) yielded significant relationships among various pigments especially between chlorophyll-*a* and fucoxanthin ( $r = 0.90$ ;  $n = 305$ ;  $p = 0.001$ ) suggesting that most of the chlorophyll-*a* biomass in the central eastern Arabian Sea is contributed by diatoms and other fucoxanthin containing prymnesiophytes. The latter remains marginally high during the post monsoon. Relation between chlorophyll-*a* and nanoflagellates was poor ( $r = 0.46$ ;  $n = 304$ ;  $p = 0.001$ ) suggesting that overall contribution from nanoflagellates was relatively small in the study area. Linear regression between chlorophyll-*a* and zeaxanthin was also significant ( $r = 0.55$ ;  $n = 314$ ;  $p = 0.001$ ) indicating the influence of cyanobacteria on chlorophyll-*a* standing stock. Dinoflagellates marker pigment peridinin also showed good correlation with chlorophyll-*a* ( $r = 0.70$ ;  $n = 168$ ;  $p = 0.001$ ) suggesting that larger phytoplankton dominate the coastal phytoplankton population in general.

(Fig. 5)

#### 4.3 Variability of halocarbons

Halocarbons showed strong short-term variability in the coastal waters of the eastern Arabian Sea (Fig. 3). The  $\text{CHCl}_3$  and  $\text{CCl}_4$  exhibited similar trends with maximal levels in the southwest monsoon. However the most interesting feature, in the present study, is the occurrence of their decreased concentrations in subsurface waters in this season. The low concentrations in near bottom waters suggest their possible consumption, including that of  $\text{CCl}_4$ , during the microbial respiration. The decomposition of halocarbons under oxygen deficient conditions has been found in the Black Sea and Saanich inlet (Tanhua et al., 1996; Lee et al., 1999) and the Gotland Basin in the Baltic Sea (Krysell et al., 1994). Under denitrifying conditions the halogenated carbon compounds have also been found to get oxidized

to carbon dioxide (Bouwer and McCarty 1983). Therefore, the coastal waters of the eastern Arabian Sea as appear to be a significant halocarbon sink in SWM. While the enhanced productivity leads to higher  $\text{CHCl}_3$  production in the surface waters its consumption in the layers below results in the vertical gradient observed. On the other hand, higher  $\text{CCl}_4$  in surface waters in the SWM season is due to heavy rainfall along the west coast of India and the subsequent freshwater discharge that is expected to be rich in its anthropogenic component. Distribution of halocarbons in the FIM and SIM seasons (Fig. 3) indicates lower levels relative to that in monsoon. Both  $\text{CHCl}_3$  and  $\text{CCl}_4$  exhibited near uniform distributions in the water column in SIM season in contrast to that observed in SWM and FIM seasons with strong vertical gradients.

$\text{CH}_2\text{Br}_2$  exhibited maxima in SWM and NEM with lowest concentrations in SIM season whereas  $\text{CHBr}_3$  was higher during the SWM. Concentrations of  $\text{CHBr}_3$  were low during SIM and NEM seasons compared to that in SWM and FIM. While the chlorocarbons exhibited maximal abundances close to the surface the bromocarbons were higher in the mid-water column (Fig. 3). Different trends in vertical and temporal distributions (Fig. 3) between chlorocarbon and bromocarbon compounds resulted possibly from different mechanisms involved in their formation and transformation. Interconversion between the two compounds in each of these individual groups could be possible depending on the dominant nature of biochemical and/or microbial processes. Considerations have been, thus, made on the conversions involving chlorobromo-compounds that ultimately yielded  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  (Moore, 2003). Our halocarbons results from the coastal Arabian Sea are quite comparable to those found elsewhere;  $\text{CH}_2\text{Br}_2$  (1-80  $\text{ng l}^{-1}$ , Klick, 1992),  $\text{CHCl}_3$  (6.0-100  $\text{ng l}^{-1}$ , Nightingale et al., 1995),  $\text{CHBr}_3$  (25-500  $\text{ng l}^{-1}$ , Klick and Abrahamsson, 1992; Dyrssen and Fogelqvist, 1981) and  $\text{CCl}_4$  (1.0-1.5  $\text{ng l}^{-1}$ , Nightingale et al., 1995). Thus short-term variations in halocarbons distribution are very pronounced in the coastal Arabian Sea. Such variability has also been found elsewhere (Dyrssen and Fogelqvist, 1985; Klick, 1992, Bravo-Linares and Mudge, 2008). Tropical oceans are known to be important source of brominated compounds to the atmosphere. Abundances of  $\text{CH}_2\text{Br}_2$  and  $\text{CHBr}_3$  from the upwelling regions off Goa are marginally higher compared to that reported by Quack et al. (2007).

Statistically significant relationships between individual groups of halocarbon compounds and with some pigments are shown in (Fig. 6). Table 2 lists statistical analyses found for all the pigments and halocarbons studied in this present attempt. Strong relation between  $\text{CH}_2\text{Br}_2$  and  $\text{CHBr}_3$  ( $r = 0.8$ ,  $n = 100$ ;  $p = 0.001$ ) suggests possible similarities in their production and occurrence however  $\text{CHCl}_3$  was

not so well correlated with the two bromocarbons (Table 2) indicating conditions of their prevalence are different. Although higher abundances of chloro- and bromo-compounds occurred almost in the same period (SWM season) their peaks were found at different times (Fig. 4). Significant relations for fucoxanthin with halocarbons, except  $\text{CCl}_4$ , suggest fucoxanthin containing prymnesiophytes and diatoms could be an important source of these compounds in coastal Arabian Sea.  $\text{CHCl}_3$  production by red microalgae *Porphyridium purpureum* and by temperate diatoms has been reported (Scarratt and Moore, 1999; Plummer and Edzwald, 2001) however  $\text{CCl}_4$  also showed good relationship with  $\text{CHCl}_3$  which is intriguing. Among the bromocarbons  $\text{CH}_2\text{Br}_2$  also showed positive correlations with few marker pigments (Table 2) indicating miscellaneous biogenic sources however correlation of  $\text{CHBr}_3$  with peridinin, zeaxanthin and nanoflagellates were low. Somewhat positive correlations between bromocarbons and pigments have been found for different oceanic basins including the Bay of Bengal (Schall et al., 1997; Yokouchi et al., 1997; Yamamoto et al., 2001). Low statistical correlations observed in some instances could be due to large external forcings, including air-sea fluxes and photochemical processes, which play vital role in determining the halocarbon abundances and their spatial and temporal variability (Quack et al., 2007).

(Fig 6 and Table 2)

In general, studies on short term variability of phytoplankton pigments and halogenated compounds in coastal waters of the central eastern Arabian Sea showed strong relationships with pigments suggesting significant production of these halogenated gases ( $\text{CHCl}_3$ ,  $\text{CH}_2\text{Br}_2$  and  $\text{CHBr}_3$ ) by marine phytoplankton in this region.

## 5 Conclusions

Short-term variability in halocarbons ( $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{CH}_2\text{Br}_2$  and  $\text{CHBr}_3$ ) was studied for the first time in the Arabian Sea along with pigment composition to find the influence of phytoplankton community on their abundances. These exhibited strong seasonality with higher production associated with summer monsoon induced upwelling related productivity. Clear vertical gradients in chlorocarbons suggest their utilization in subsurface waters under the oxygen deficient conditions. As the Arabian Sea is the most productive region of the Indian Ocean where the halocarbon consumption under low oxygen conditions in the water column assumes significance, as suggested by our present results, this region is potentially important for the turnover of halocarbons in the oceans.

## Acknowledgement

The author would like to thank NIO/CSIR for awarding CSIR research fellowship and Mr Hanumant Dalvi for his help in sampling. The author would also like to acknowledge the support provided by Dr. S.W.A Naqvi and Dr. M. Dileep Kumar during this work. This work formed a part of the CSIR-supported Network Project CMM0009 and NWP0014.

## References

- Abrahamsson, K., Klick, S., 1990. Determination of biogenic and anthropogenic volatile halocarbons in sea water by liquid-liquid extraction and capillary gas chromatography. *Journal of Chromatography* 513, 39-45.
- Abrahamsson, K., Choo, K.S., Pedersen, M., Johansson, G., Snoeijs, P., 2003. Effect of temperature on the production of hydrogen peroxide and volatile halocarbons by brackish- water algae. *Phytochemistry* 64, 725-734
- Baker, A.R., Turner, S.M., Broadgate, W.J., Thompson, A., McFiggans, G.B., Vesperii, O., Nightengale, P.D., Liss, P.S., Jickells, T.D., 2000. Distribution and sea– air fluxes of biogenic trace gases in the eastern Atlantic Ocean. *Global Biogeochemical Cycles* 14, 871– 886.
- Bange, H.W., Ramesh, R., Rapsomanikis, S., Andreae, M.O., 1998. Methane in surface waters of the Arabian Sea. *Geophysical Research Letters* 25, 3547–3550.
- Barlow, R., V. Stuart., V. Lutz., H. Sessions., S. Sathyendranath., T. Platt., M. Kyewalyanga., L. Clementson ., M. Fukasawa., S. Watanabe., Devred, E., 2007. Seasonal pigment patterns of surface phytoplankton in the subtropical southern hemisphere. *Deep- Sea Research I* 54, 1687-1703.
- Barlow, R.G., Mantoura, R.F.C., Cummings, D.G., 1999. Monsoonal influence on the distribution of phytoplankton pigments in the Arabian Sea, *Deep-Sea Research II* 46, 677-699.
- Barlow, R.G., Sessions, H., Balarin, M., Weeks, S., Whittle, C., Hutchings, L., 2005. Seasonal variation in phytoplankton in the southern Benguela: pigment indices and ocean colour. *African Journal of Marine Sciences* 27, 275-288.
- Bell, N., Hsu, L., Jacob, D.J., Schultz, M.G., Blake, D.R., Butler, J.H., King, D.B., Lobert, J.M., Maier-Reimer, E., 2002. Methyl iodide: Atmospheric budget and use as a tracer of marine convection in global models. *Journal of Geophysical. Research* 107, ACH 8-1-ACH 8-12.
- Bouwer, E.J., McCarty, P.L., 1983. Transformation of 1-carbon and 2-carbon halogenated aliphatic organic compounds under methanogenic conditions. *Applied Environmental Microbiology* 45, 1286-1294

- Bravo-Linares, C.M., Mudge, S.M., 2008. Temporal trends and identification of the sources of volatile organic compounds in coastal seawater. *Journal of Environmental Monitoring* 11, 628-641.
- Christof, O., Seifert, R., Michaelis, W., 2002. Volatile halogenated organic compounds in European estuaries. *Biogeochemistry* 59, 143-160.
- Carpenter, L.J., Wevill, D.J., Palmer, C.J., Michels, J., 2007. Depth profiles of volatile iodine and bromine –containing halocarbons in coastal Antarctic waters. *Marine Chemistry* 103, 227-236.
- Class, T., & Ballschmiter K., 1988. Chemistry of organic traces in air VIII: Sources of bromo- and bromochloromethane in marine air and surface water of the Atlantic Ocean. *Journal of Atmospheric Chemistry*. 6, 35-46.
- Dyrssen D., Fogelqvist, E. 1981. Bromoform concentrations of the Arctic ocean in the Svalbard area. *Oceanology Acta* 4, 313-317.
- Dyrssen D., Fogelqvist, E., Krysell, M., Sturm, R., 1990. Release of halocarbons from an industrial estuary. *Tellus* 42 b, 162-169.
- Elliott, S., Rowland, F. S., 1995. Methyl halide hydrolysis rates in natural waters. *Journal of Atmospheric Chemistry*. 20, 229-236.
- Fogelqvist, E., 1985. Carbontetrachloride.Tetrachloroethylene.1, 1, 1-trichloroethane and bromoform in Arctic sea water. *Geophysical Research Letters* 90, 9181-9193.
- Gauns, M., Mohanraju, R., Madhupratap, M., 1996. Studies on macrozooplankton from central and eastern Arabian Sea. *Current Science*.71, 874-877.
- Goodwin, K. D., Lidstrom, M. E., Oremland, R. S., 1997. Marine bacterial degradation of brominated methanes. *Environmental Science and Technology* 31, 3188-3192.
- Happell, J.D., Wallace, D.W.R., 1996. Methyl iodide in the Greenland/Norwegian Seas and the tropical Atlantic Ocean: Evidence for photochemical production, *Geophysical Research Letters* 23, 2105 – 2108.
- Jayakumar, D.A., S.W.A. Naqvi., Narvekar, P.V., George, M.D., 2001.Methane in coastal and offshore waters of the Arabian Sea. *Marine Chemistry* 74, 1-13.
- King D. B. and Saltzman E. S., 1997. Removal of methyl bromide in coastal seawater: Chemical and biological rates. *Journal Geophysical Research* 102, 18715-18721.
- Klick, S., 1992. Seasonal variations of biogenic and anthropogenic halocarbons in seawater from a coastal site. *Limnology Oceanography* 37,1579-1585.
- Klick, S., K. Abrahamsson., 1992. Biogenic volatile iodated hydrocarbons in the ocean. *Journal of Geophysical Research* 97, 12683-12687.

- Krysell, M., Nightingale, P.D., 1994. Lower molecular weight halocarbons in the Humber and Rhine estuaries determined using a new purge and trap gas chromatography method. *Continental Shelf Research* 14, 1311-1329.
- Latasa, M., Bidigare, R.R., 1998. A comparison of phytoplankton population of the Arabian Sea during the Spring Intermonsoon and Southwest Monsoon of 1995 as described by HPLC- analyzed pigments. *Deep-Sea Research II* 45, 2133-2170.
- Laternus, F., Wiencke, C., Kloser, H., 1996. Antarctic macroalgae –sources of volatile halogenated organic compounds. *Marine Environmental Research* 41,169-181.
- Lee, B-S., Bullister, J.L., Whitney, F.A., 1999. Chlorofluorocarbon CFC-11 and carbon tetrachloride removal in Saanich Inlet, an Intermittently Anoxic Basin. *Marine Chemistry* 66, 171–185.
- Lovelock, J.E., 1975. Natural halocarbons in the air and in the sea. *Nature*, 256, 193-194.
- Manley, S.L., Goodwin, K and North, W. J., 1992. Laboratory production of bromoform, methylene bromide, and methyl iodide by macroalgae and distribution in near shore California waters. *Limnology Oceanography* 37, 1652-1659.
- Moore, R.M., O, Zafiriou., 1994. Photochemical production of methyl iodide in seawater. *Journal of Geophysical Research* 99, 16415-16420.
- Moore, R.M., Webb, M.E., 1996. The relationship between methyl bromide and chlorophyll *a* in high-latitude ocean waters. *Geophysical Research Letters* 23, 2951-2954.
- Moore, R.M., (2003). Marine sources of volatile organohalogenes. In: (Ed.): *Handbook of Environmental Chemistry* 3(P), 85-101.
- Mtolera, M. S. P., Collen J., Pedersen M., Ekdahl A., Abrahamsson K., and Semesi A. K., 1996. Stress-induced production of volatile halogenated organic compounds in *Eucheuma denticulatum* (Rhodophyta) caused by elevated pH and high light intensities. *European Journal of Phycology* 31, 89-95.
- Naqvi, S.W. A., Jayakumar, D. A., Narvekar, P. V., Naik, H., Sarma, V. V. S. S., D' Souza, W., Joseph, S., and George, M. D., 2000. Increased marine production of N<sub>2</sub>O due to intensifying anoxia on the Indian continental shelf. *Nature* 408, 346–349.
- Naqvi, S. W. A, Naik, H., Jayakumar, D. A., Shailaja, M. S., Narvekar, P. V., 2006a. Seasonal oxygen deficiency over the western continental shelf of India, in: *Past and Present Water Column Anoxia*. NATO Science Series, IV. Earth and Environmental Sciences Vol 64, Springer, 195–224.
- Nightingale, P.D., Malin, G., Liss, P.S., 1995. Production of chloroform and other low molecular-weight halocarbons by some species of macroalgae. *Limnology Oceanography* 40, 680 – 689.

- Paraba, S. G., Matondkara, S.G. P., Gomes, H. do R., Goes, J.I., 2006. Monsoon driven changes in phytoplankton populations in the eastern Arabian Sea as revealed by microscopy and HPLC pigment analysis. *Continental Shelf Research* 26, 2538-2558.
- Patra, P.K., Lal, S., Venkataramani, S., Gauns, M., Sarma, V.V.S.S., 1998. Seasonal variability in distribution and fluxes of methane in the Arabian Sea. *Journal of Geophysical Research* 103, 1167-1176.
- Plummer, J. D., Edzwald, J. K. 2002. Effects of chlorine and ozone on algal cell properties and removal of algae by coagulation. *Journal of Water Supply Research Technology* 51, 307-318.
- PrasannaKumar, S., Ramaiah, N., Gauns, M., Sarma, V.V.S.S., Muraleedharan, P.M., Raghukumar, S., Dileep Kumar, M., Madhupratap, M., 2001. Physical forcing of biological productivity in the northern Arabian Sea during northeast monsoon. *Deep-Sea Research II* 48, 1115-1126.
- Quack, B., Wallace, D.W., 2003. Air-sea flux of bromoform: Controls, rates and implications. *Global Biogeochemical Cycles* 17, 1023.
- Quack, B., I. Peeken., G. Petrick., K. Nachtigall., 2007. Oceanic distribution and source of bromoform and dibromomethane in Mauritanian upwelling. *Journal of Geophysical Research* 112, C10006.
- Ramaiah, N., Raghukumar, S., and Gauns, M., 1996. Bacteria abundance and production in central and eastern Arabian Sea. *Current Science* 71, 878-882.
- Rasmussen, R.A., M.A.K. Khalil, R. Gunawardan., S.D. Hoyt., 1982. Atmospheric methyl iodide (CH<sub>3</sub>I). *Journal of Geophysical Research* 87, 3086-3090.
- Rensburg, J. F. J. V., Van Huyssteen, J. J. and A. J. Hasse'rt., 1978. A semi- automated technique for the routine analysis of volatile organohalogens in water purification processes. *Water Research* 12v, 127 -131.
- Richter, U., Wallace D.W.R., 2004. Production of methyl iodide in the tropical Atlantic Ocean. *Geophysical Research Letters* 31, L23S03.
- Roy, R., Prathihary, A., G. Mangesh., S.W.A Naqvi., 2006. Spatial variation of phytoplankton pigments along the southwest coast of India. *Estuarine Coastal Shelf Science* 69, 189-195.
- Russo, M.V., L. Campanella, P. Avino., 2003. Identification of halocarbons in the Tiber and Marta River by static headspace and liquid-liquid extraction analysis. *Journal of Separation Science* 26, 376-380.
- Salawitch R. J., 2006. Atmospheric chemistry: Biogenic bromine. *Nature*. 439, 275-277.
- Sarma, V.V.S.S., Dileep, George, M.D., 1998. The central and the eastern Arabian Sea as perennial source of atmospheric carbondioxide. *Tellus* 50B, 179-184.

- Sawant S, Madhupratap, M., 1996. Seasonality and composition of phytoplankton in Arabian Sea. *Current Science* 71, 869-873.
- Scarratt, M.G. and Moore, R.M., 1996. Production of methyl chloride and methyl bromide in laboratory cultures of marine phytoplankton. *Marine Chemistry* 54, 263-272.
- Scarratt, M.G., R.M. Moore., 1998. Production of methyl bromide and methyl chloride in laboratory cultures of marine phytoplankton II. *Marine Chemistry* 59, 311-320.
- Scarratt, M.G., R.M. Moore., 1999. Production of Chlorinated Hydrocarbons and Methyl Iodide by the Red Microalga *Porphyridium purpureum*. *Limnology Oceanography* 44, 703-707.
- Schall, C., Heumann, K.G., Kirst, G.O., 1997. Biogenic volatile organoiodine and organobromine hydrocarbons in the Atlantic Ocean from 42 °N to 72 °S. *Fresenius Journal of Analytical Chemistry* 359, 298-305.
- Shankar, D., Vinayachandran, P.N., Unnikrishnan, A.S., 2002. The monsoon currents in the north Indian Ocean. *Progress in Oceanography* 52, 63-120.
- Shenoy, D.M., Kumar, M.D., 2007. Variability in abundance and fluxes of dimethyl sulphide in the Indian Ocean. *Biogeochemistry* 83, 277-292.
- Shetye, S.R., 1998. West India coastal current and Lakshadweep high/low. *Sadhana* 23, 637-651.
- Singh, H.B., Salas, L.J., and Stiles, R.E., 1983. Selected man-made halogenated chemicals in the air and oceanic environment. *Geophysical Research Letters* 88, 3675-3683.
- Tait. V. K., Moore, R.M., 1995. Methyl chloride (CH<sub>3</sub>Cl) production in phytoplankton cultures. *Limnology Oceanography* 40, 189-195.
- Tanhua, T., Fogelqvist, E., Basturk, O., 1996. Reduction of volatile halocarbon in anoxic seawater, results from a study in the Black sea. *Marine Chemistry* 54, 159-170.
- Tokarczyk, R., Moore, R.M., 1994. Production of volatile organohalogen by marine phytoplankton, *Geophysical Research Letters* 21, 285-288.
- Upstill-Goddard R. C., Barnes J., Owens, N. J. P., 1999. Nitrous oxide and methane during the 1994 SW monsoon in the Arabian Sea/northwestern Indian Ocean. *Journal of Geophysical Research* 104, 30067-30084.
- Van Heukelem. (2002). HPLC phytoplankton pigments: Sampling, laboratory methods, and quality assurance procedures. In: Mueller, J., and Fargion, G., (Eds.), *Ocean Optics Protocols for Satellite Ocean Color Sensor, Revision 3, Volume 2, Chapter 16, NASA Technical Memorandum 2002-2004*, pp.258-268.



- Vidussi, F., Claustre, H., Manca, B., Luchetta, A., & Marty, J.C., 2001. Phytoplankton pigment distribution in relation to the upper thermocline circulation in the Eastern Mediterranean Sea during winter. *Journal of Geophysical Research* 106, 19939-19956.
- Wever, R., Tromp, M. G. M., Krenn, B. E., Marjani, A., and Vantol, M., 1991. Brominating activity of the seaweed *Ascophyllum-nodosum* – impact on the biosphere, *Environmental Science and Technology* 25, 446–449.
- Yang, X., Cox, R.A., Warwick, N.J., Pyle, J.A., Carver, G.D., O' Connor, F.M., Savage, N.H., 2005. Tropospheric bromine chemistry and its impacts on ozone: a model study. *Journal of Geophysical Research* 110, D23311.
- Yamamoto, H., Y. Yokouchi., A. Otsuki., H. Itoh., 2001. Depth profiles of volatile halogenated hydrocarbons in seawater in the Bay of Bengal. *Chemosphere* 45, 371-377.
- Yokouchi, Y., Mukai, H., Yamamoto, H., Otsuki, A., Saitoh, C., Nojiri, Y., 1997. Distribution of methyl iodide, ethyl iodide, bromoform and dibromomethane over the ocean (east and southeast Asian seas and the western Pacific). *Journal of Geophysical Research* 102 (D7), 8805-8809.
- Yokouchi, Y., N. Yujihiro., L.A. Barrie., D. Toom-Sauntry., Y. Fujinuma., 2001. Atmospheric methyl iodide: High correlation with surface sea-water temperature and its implication on the sea-to-air-flux. *Journal of Geophysical Research* 106, 12661-12668.
- Zafiriou, O.C., 1974. Photochemistry of halogens in the marine atmosphere. *Journal of Geophysical Research* 79, 2730 – 2732.
- Zoccolillo, L., Abete, C., Amendola, L., Ruocco, R., Andrea, S., Termine, M., 2004. Halocarbons in aqueous matrices from the Rennick glacier and the Ross Sea (Antarctica). *International Journal of Environmental and Analytical Chemistry* 84 (6-7), 513-522.

Table 1: Pigment and diagnostic indices used to find phytoplankton communities (after Barlow et al. (2007)).

Table 2: Correlation matrix among the phytoplankton pigments and halogenated carbons. Bold values indicate significant levels ( $p < 0.05$ ).

Fig. 1. Candolim Time Series (CaTS) station (G1 to G5) locations in coastal waters of the central eastern Arabian Sea off Goa.

Fig. 2. Variability in the abundances ( $\text{ng l}^{-1}$ ) of phytoplankton pigments at CaTS station G5 in the coastal Arabian Sea. July 2005 and the period of May to July 2006 could not be covered due to rough monsoon conditions and our summer monsoon expeditions, respectively and red colour post represent extrapolated data.

Fig. 3. Vertical variations in Diagnostic Indices of diatoms, nanoflagellates, cyanobacteria (prokaryotes) and dinoflagellates from April 2005 to August 2007 at Station G5. Shown on the right are the average percent contributions (for the study period) of four phytoplankton groups derived from pigment analyses and diagnostic indices.

Fig. 4. Variability in the abundances ( $\text{ng l}^{-1}$ ) of  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{CH}_2\text{Br}_2$  and  $\text{CHBr}_3$  at station G 5 in coastal Arabian Sea. Missed data for May to July 2006 is for the reason detailed in Fig. 2. Between December 2005 and April 2006 only surface and near bottom samples were studied for chlorocarbons.

Fig. 5. Relationships found between chlorophyll *a* and a) fucoxanthin (higher values are when upwelling occurred), b) nanoflagellates index, c) peridinin, d) zeaxanthin (higher values occurred during March and April due to increase in cyanobacterial species) and e) diagnostic pigment (DP, see Table 1).

Fig. 6. Relationships among halocarbon and pigments for coastal waters (along CaTS section) off Goa.

**Table 1**

Symbol	Pigment	Designation
DP	Diagnostic pigments	Allo+But+Chlb+Fuc+Hex+Per+Zea+Per
Diat <sub>DP</sub>	Diatom proportion of DP	Fuc/DP
Dino <sub>DP</sub>	Dinoflagellaets proportion of DP	Per/DP
Flag <sub>DP</sub>	Flagellate proportion of DP	(Allo+But+Chlb+Hex)/DP
Prok <sub>DP</sub>	Prokaryote proportion of DP	Zea/DP

**Table 2**

Variables	Chl a	Fuc	Per	Zea	19HF+19BF+Allo+Chl b	CHCl <sub>3</sub>	CCl <sub>4</sub>	CH <sub>2</sub> Br <sub>2</sub>	CHBr <sub>3</sub>
Chl a	1.00								
Fuc	<b>0.90</b>	1.00							
Peridinin	<b>0.70</b>	-0.05	1.00						
Zeaxanthin	<b>0.55</b>	0.37	0.02	1.00					
19HF+19BF+Allo+Chl b	0.46	0.34	0.06	0.13	1.00				
CHCl <sub>3</sub>	0.43	<b>0.93</b>	0.40	0.44	<b>0.54</b>	1.00			
CCl <sub>4</sub>	0.09	0.01	-0.10	-0.13	-0.01	<b>0.81</b>	1.00		
CH <sub>2</sub> Br <sub>2</sub>	<b>0.66</b>	<b>0.58</b>	<b>0.59</b>	<b>0.65</b>	<b>0.72</b>	<b>0.62</b>	-0.15	1.00	
CHBr <sub>3</sub>	<b>0.53</b>	<b>0.75</b>	0.30	0.17	0.33	<b>0.56</b>	-0.04	<b>0.80</b>	1.00

Figure 1

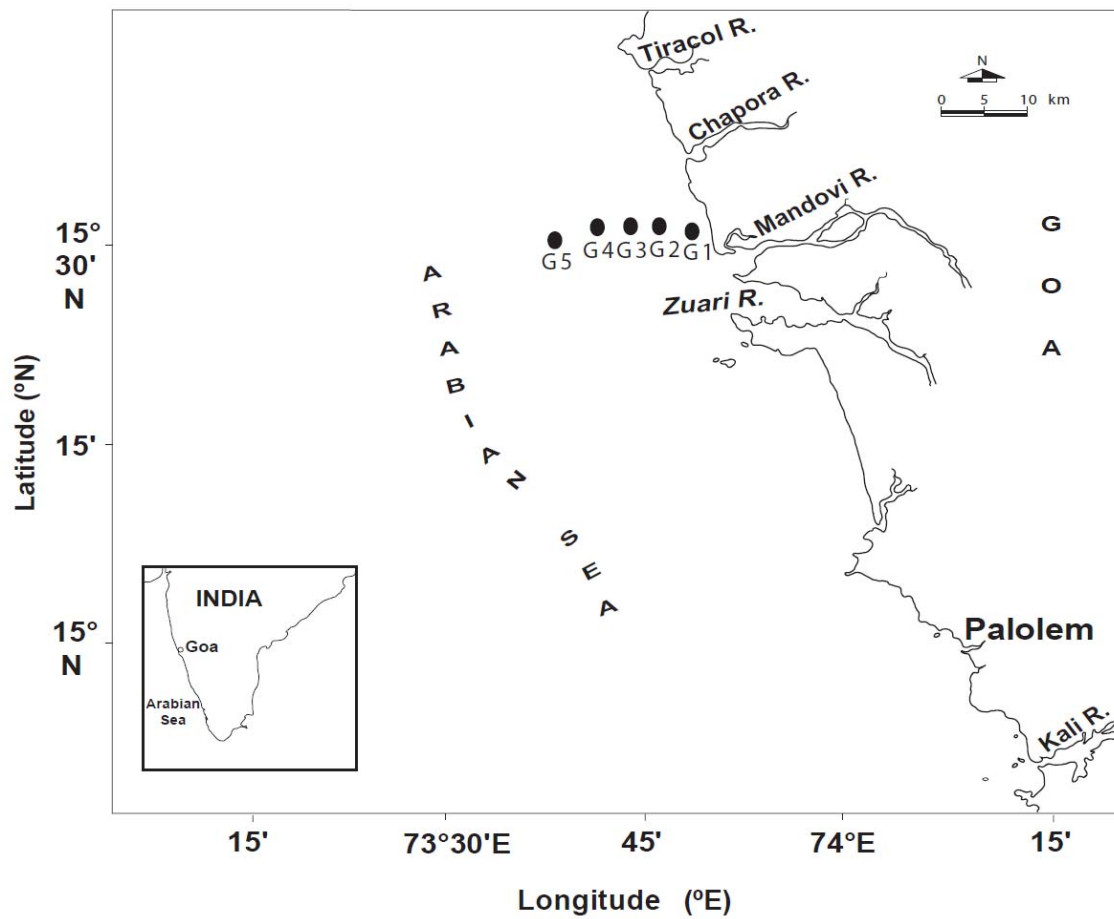


Figure 2

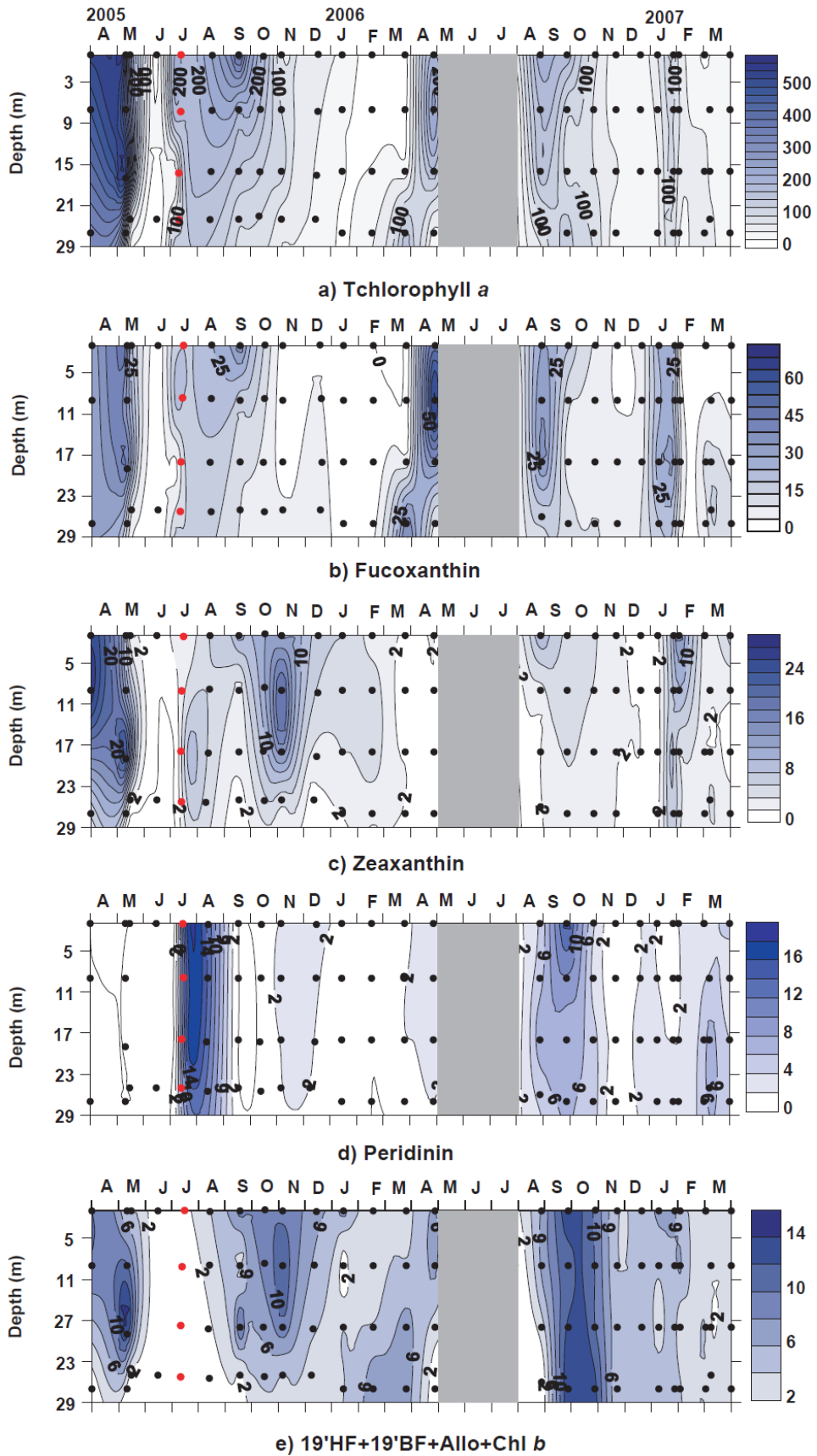


Figure 3

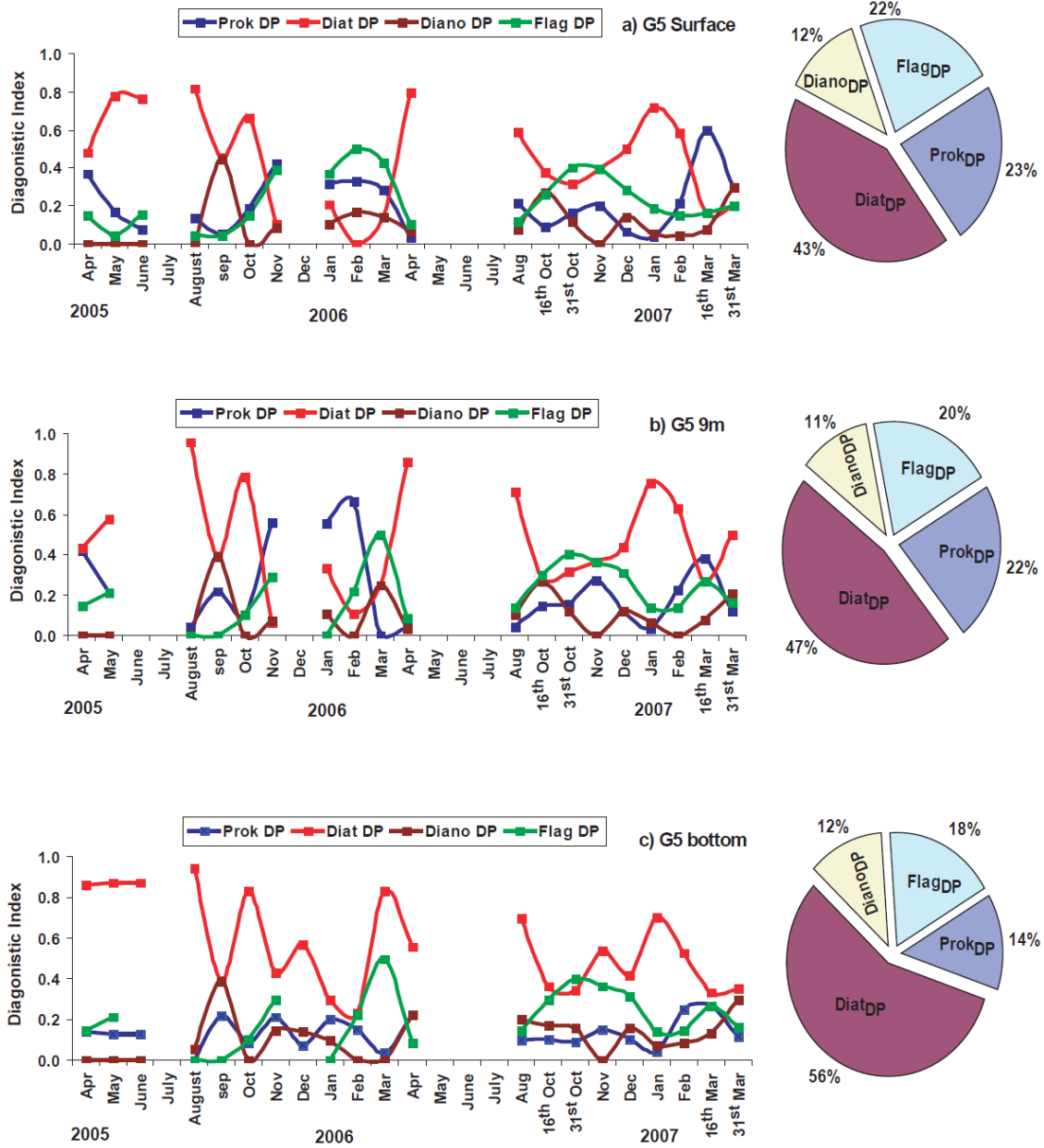
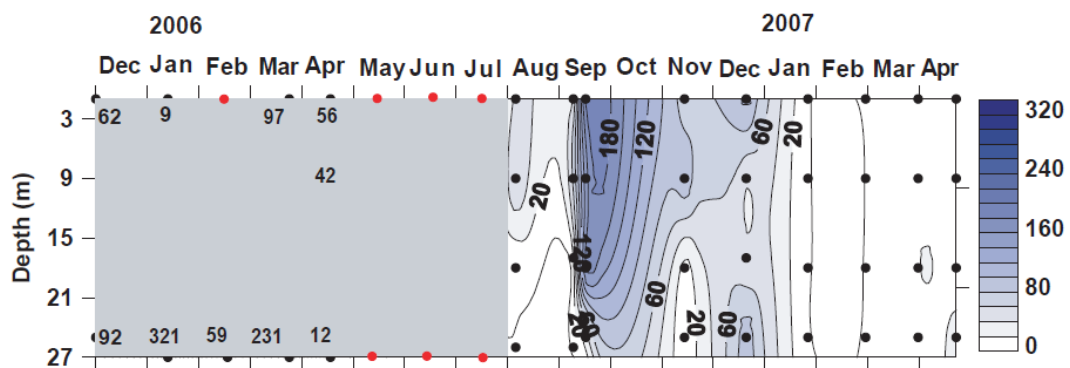
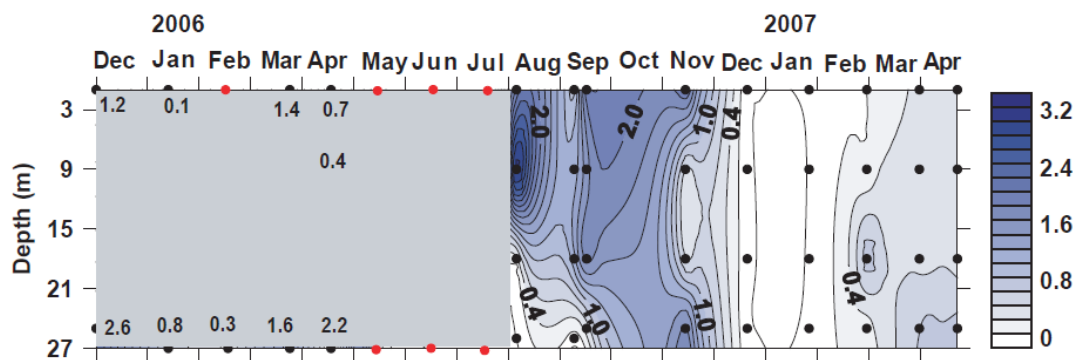


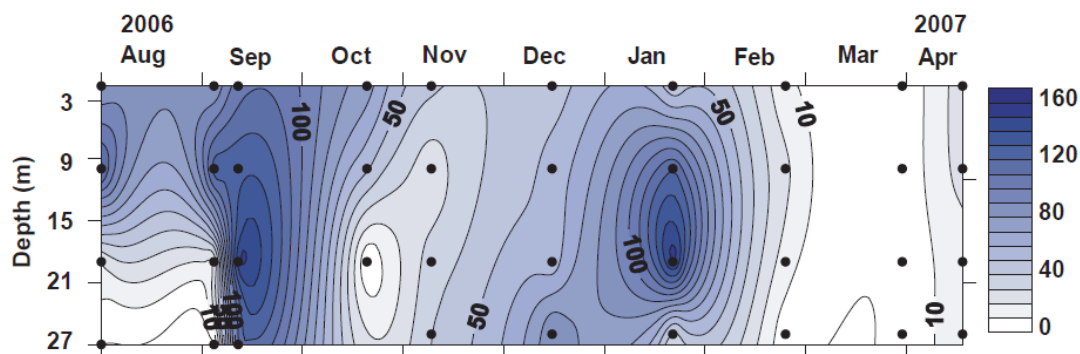
Figure 4



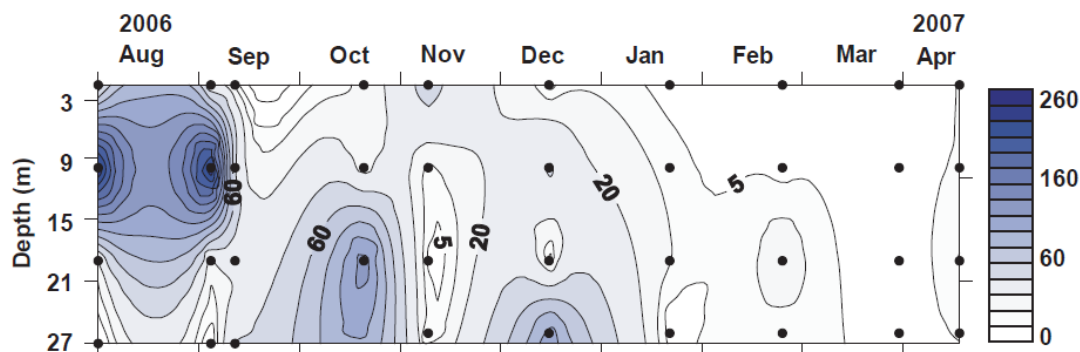
a)  $\text{CHCl}_3$



b)  $\text{CCl}_4$



c)  $\text{CH}_2\text{Br}_2$



d)  $\text{CHBr}_3$

Figure 5

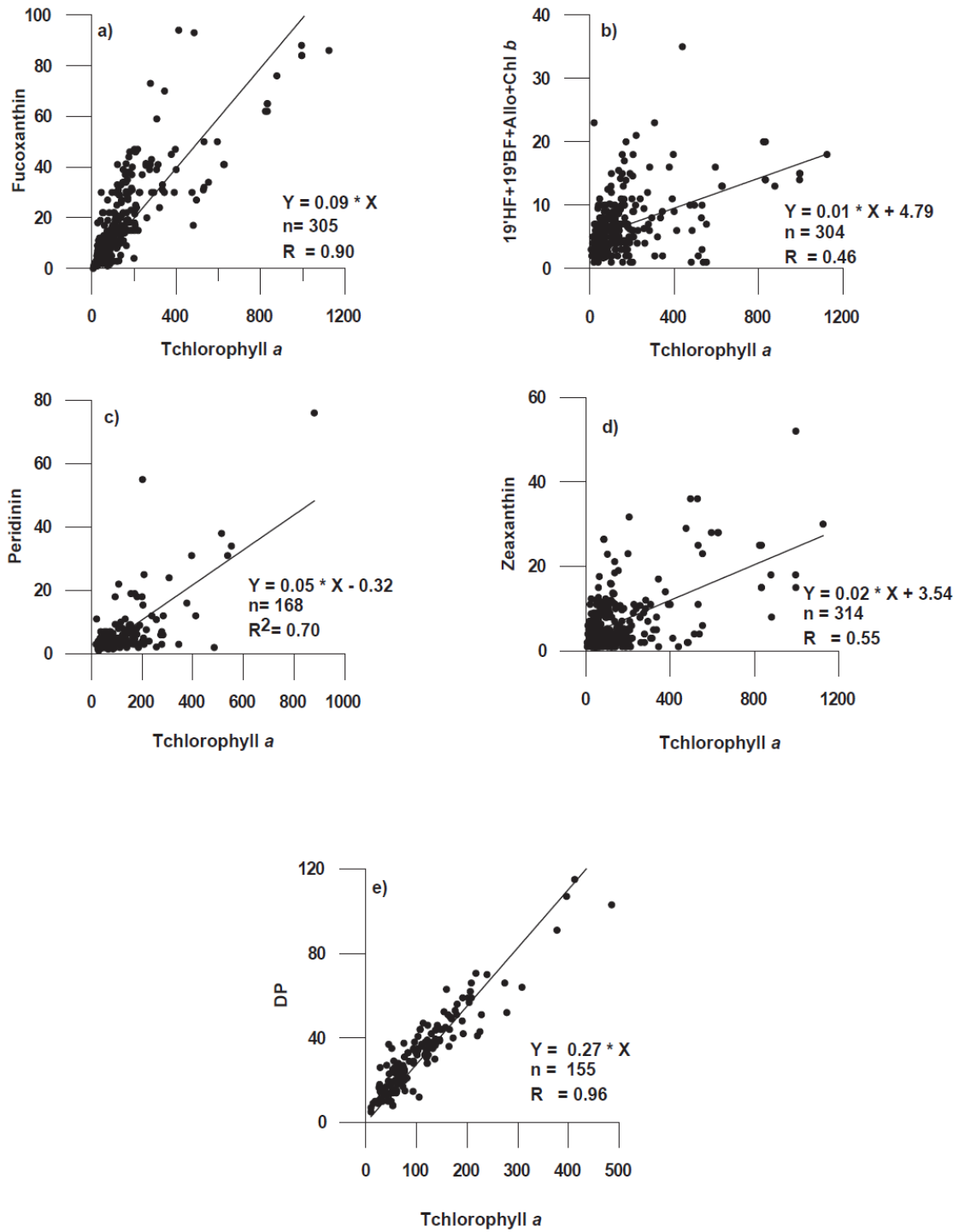




Figure 6

