

A study of volatile halocarbons in relation to phytoplankton pigments during a *Trichodesmium* bloom in the coastal eastern Arabian Sea

Rajdeep Roy*; Anil Pratihary; Gayatree Narvenkar; Sunita Mochemadkar; Mangesh Gauns and S.W.A. Naqvi

Affiliation: National Institute of Oceanography, Council of Scientific & Industrial Research, Dona Paula, Goa 403004, India

*Corresponding author:

Phone: +91-832-2450669; **Fax:** +91-832-2450607; **Email:** rajdeepro2003@yahoo.com

Abstract

Eukaryotic phytoplankton such as diatoms and prymnesiophytes are known to produce biogenic halocarbons in the ocean that serve as important sources of chlorine and bromine to the atmosphere, but the role of cyanobacteria in halocarbon production is not well established. We studied distributions of chloroform (CHCl_3), carbon tetrachloride (CCl_4), methylene bromide (CH_2Br_2) and bromoform (CHBr_3) in relation to phytoplankton composition, determined from pigment analysis complemented by microscopic examination, for one month in coastal waters of the eastern Arabian that experienced a *Trichodesmium* bloom that typically occurs during the Spring Intermonsoon season. High concentrations of zeaxanthin ($23 \mu\text{g l}^{-1}$), alpha beta betacarotene ($6 \mu\text{g l}^{-1}$) and chlorophyll *a* ($67 \mu\text{g l}^{-1}$) were found within the bloom whereas the marker pigment concentrations were low outside the bloom. CHCl_3 and CCl_4 occurred in relatively high concentrations in surface waters whereas CH_2Br_2 and CHBr_3 were restricted to the subsurface layer. Chlorinated halocarbons were positively correlated among themselves and with CHBr_3 . The observed spatial and temporal trends in brominated compounds seem to be related to the abundance of *Trichodesmium* even though correlations between concentrations of brominated compounds with various marker pigments were poor and statistically insignificant. The results support the existence of multiple sources and sinks of halogenated compounds, which might mask the relationship between halocarbons and phytoplankton composition.

Keywords: Phytoplankton composition, photosynthetic pigments, *Trichodesmium*, halocarbons, Arabian Sea, Indian coast

Introduction

Phytoplankton are known to produce various halocarbon compounds that are environmentally important because of their greenhouse warming potential and ability to destroy ozone in the stratosphere (Lovelock et al., 1975; Salawitch, 2006; Quack and Wallace, 2003). Oceanic fluxes of biogenic halocarbons contribute significantly to the atmospheric halocarbon budgets (Abrahamsson et al., 2004). The long-lived bromine- and chlorine-containing species are particularly important as they are involved in stratospheric ozone depletion (Chameides and Davis, 1980). Production of these compounds by phytoplankton is species-dependent (Tokarczyk and Moore, 1994). However, in addition to production by phytoplankton (Singh et al., 1983; Tokarczyk and Moore, 1994; Tait and Moore, 1995; Moore et al., 1996; Scarratt and Moore, 1998) and macro algae (Ek Dahl et al., 1998; Manley et al., 1992), anthropogenic activities could also be the source of these compounds in the coastal areas (Mills et al., 1998; Christof et al., 2002) making it difficult to identify their origin. Nevertheless, co-variation of halogenated compounds and photosynthetic pigments has been taken to support their production by autotrophs (Schall et al., 1997; Yamamoto et al., 2001; Bravo-Linares and Mudge, 2008; Quack et al., 2007). Production of brominated and chlorinated methanes in the open ocean has often been linked to phytoplankton, particularly diatoms (Baker et al., 2000; Klick and Abrahamsson, 1992; Class and Ballschmiter, 1988; Plummer & Edzwald, 2002).

Unlike eukaryotic phytoplankton and macroalgae, information on halocarbon production by cyanobacteria is quite limited. A recent study by Karlsson et al. (2008) has demonstrated the potential of cyanobacteria in the Baltic Sea in the production of halogenated (especially brominated) compounds. *Trichodesmium* is inarguably the best known of all cyanobacterial genera in the ocean. However, little is known about the halocarbon production by this genus, which occurs widely in tropical waters often forming large blooms. These blooms are, however, quite patchy, both temporally and spatially. The patchy distribution is usually connected to the physical characteristics of surface waters (Kononen and Leppanen 1997). In the Arabian Sea, for example, *Trichodesmium* blooms are mostly confined to the Spring Intermonsoon (SI) period (Qasim, 1970; Devassy et al., 1979; Capone et al., 1998; Poulton, 2009; Krishnan et al., 2007). The high surface temperature, calm weather and oligotrophic conditions in surface waters seem to favour growth of *Trichodesmium* during the SI season (Sen Gupta and Naqvi, 1984). In order to study the hitherto unknown potential of *Trichodesmium* in halocarbon production, we carried out a study of phytoplankton pigments and halocarbons (CHCl_3 , CCl_4 , CH_2Br_2 and CHBr_3) in the eastern Arabian Sea for one month during this season the results of which are presented here.

2.0 Materials and methods

A patchy *Trichodesmium* bloom was observed between 3rd and 5th April 2007 during regular visits to the Candolim Time Series (CaTS) station G3 located in the eastern Arabian Sea off Goa, India (Figure 1a). In order to investigate the phenomenon in detail and to extend the observations further offshore, three cruises of the coastal research vessel *Sagar Sukti* (SaSu) were undertaken: SaSu 135 from 17th to 18th April., SaSu 139 from 4th to 5th May and SaSu 141 from 10th to 11th May 2007. The bloom was found to extend up to Sta. G8. Monthly composite images of chlorophyll (Chl *a*) and sea surface temperature (SST) prepared with the MODIS data (<http://daac.gsfc.nasa.gov/giovanni>) are shown in Fig. 2.

Niskin bottles (5 L) fixed on polyvinyl chloride (PVC)-coated hydrowire were used for sampling of water for routine measurements as well as for halocarbons and phytoplankton pigments.

(Insert Figure 1)

2.1 Halocarbons extraction

Subsamples for halocarbons were collected immediately after subsampling for oxygen in 100-ml volumetric flasks by following the standard protocol for dissolved gases, i.e. bubbling was avoided and 200-300 ml of water was allowed to overflow. Triplicate samples were taken during 3rd-5th April but only one sample was collected subsequently from each depth. Samples were preserved immediately at 4°C in dark until extraction. Halocarbons extraction was carried out following the procedure of Abrahamsson and Klick (1990). For checking the detection limit water was purged with ultra pure grade nitrogen (purity 99.999%) and analyzed for any background contamination. Detection limits, which is defined here as signal to noise ratio (S/N=5), were determined by spiking the N₂-purged water with the halogenated compounds being analyzed. The precision was determined as the relative standard deviation of quadruplicate analyses of the spiked samples. The detection limit ranged from 0.01 and 1.2 ng l⁻¹ while the precision varied between 7.2 and 9.7%. The lowest detection limit was for the chlorinated compounds (CHCl₃ and CCl₄) whereas it was the highest for dibromomethane. Bromoform could be detected at 0.3 ng l⁻¹. A 4-5 point external standard calibration (ESTD) was performed by using pure liquid standards obtained from Sigma Aldrich (Germany). The peak area verses amount of standard (dissolved in methanol (Chromasolv) procured from E. Merck) injected was used to prepare calibration curves. Linearity through the origin was assumed and average calibration factor was taken for quantification. Further details of the method have been presented in Roy (2010).

2.2 Pigments extraction and speciation

For the analysis of phytoplankton pigments water samples (10-800 ml) were filtered through Whatman GF/F (25 mm, 0.7 μm) filters that were stored at -85°C until analysis. Extraction of pigments was done in 3 ml of 100% acetone for 5 min in an ultrasonic bath filled with ice-water. The extracts were stored overnight at -20°C until analysis. The HPLC analysis was carried out following the method of Roy et al. (2006) however the buffer used was tetra butyl ammonium acetate and had a concentration of 28 milimolar. The method did not separate alpha and betacarotene and hence these compounds were grouped together. We also used the weighted sum of different marker pigments as proposed by Utiez et al. (2006) to reconstruct the proportion of various phytoplankton groups for this study. The sum of 19'-hexanoyloxyfucoxanthin (19'HF), 19'-butanoyloxyfucoxanthin (19'BF), and alloxanthin (Allo) was used to indicate nanoflagellates abundance where as the sum zeaxanthin (Zea) and chlorophyll *b* (Chl *b*) have been used to represent picoplankton group. Microplankton population was represented by the sum of fucoxanthin (Fuco) and peridinin (Perid). It should be noted that these pigment grouping reported here does not strictly represent the true size class and has already been acknowledged by several authors (Vidussi et al., 2001, Roy et al., 2006; Utiz et al., 2006). For calculating the sum of all weighted diagnostic pigments, $\sum\text{DPw}$, expressed as:

$$\begin{aligned}\sum\text{DPw} = & 1.41 [\text{Fuco}] + 1.41 [\text{Perid}] + 1.27 [19'\text{HF}] \\ & + 0.35 [19'\text{BF}] + 0.60 [\text{Allo}] + 1.01 [\text{Chl } b] \\ & + 0.86 [\text{Zea}]\end{aligned}$$

In comparison to DP, $\sum\text{DPw}$ represents the chlorophyll *a* concentration, which can be reconstructed from the knowledge of the concentration of the seven other pigments (Utiz et al., 2006). The fractions of the chlorophyll *a* concentration associated with each of the three phytoplankton classes (f_{micro} , f_{nano} and f_{pico}) are then derived according to the following ratios.

$$f_{\text{micro}} = (1.41 [\text{Fuco}] + 1.41 [\text{Perid}]) / \sum\text{DPw}$$

$$f_{\text{nano}} = (1.27 [19'\text{HF}] + 0.35 [19'\text{BF}] + 0.60 [\text{Allo}]) / \sum\text{DPw}$$

$$f_{\text{pico}} = (1.01 [\text{Chl } b] + 0.86 [\text{Zea}]) / \sum\text{DPw}$$

We used these ratios to derive the proportions of the three groups for our sampling period. For the qualitative and quantitative analyses of phytoplankton (>5 μm), 250 ml of sea water samples were collected and fixed with acid Lugol's iodine (1% w/v) and preserved in 3% formalin solution. The samples were stored in dark at low temperature (4°C) until enumeration. The settling and siphoning procedure was followed to obtain 50 ml concentrate. Analyses of this concentrate was carried out in triplicate by mounting 1 ml on a Sedgwick Rafter counting chamber and examining through an Olympus inverted microscope (magnification 100-200X). Generic and species identifications were done according to various taxonomic keys following Subrahmanyam (1959), Lebour (1978) and Tomas (1996).

3. Result

3.1 Variability of phytoplankton pigments

Satellite data for the period February-May 2007 show gradual warming in the central Arabian Sea (Figure 2) with systematic decline in the chlorophyll *a* concentration following the cessation of the phytoplankton bloom caused by convective mixing in winter. In general, the SI period (April-May) is characterized by oligotrophic condition (Figure 2) in the central Arabian Sea which favors the development of cyanobacterial blooms such as the *Trichodesmium* bloom that was observed by us off the central west coast of India during April-May 2007. The waters affected by the bloom were distinguished by high concentrations of marker pigments zeaxanthin (23 $\mu\text{g l}^{-1}$), alpha and betacarotene (6 $\mu\text{g l}^{-1}$) and chlorophyll *a* (67 $\mu\text{g l}^{-1}$) (Figure 1a). Apart from *Trichodesmium*, other phytoplankton groups, especially diatoms, were also present in large numbers at depths below the bloom. The major diatom species at G3 were *Bacteriastrum furcatum* (range 0-10500 cells l^{-1}), *Chaetoceros curvisetus* (5456-24173 cells l^{-1}) and *Leptocylindrus minimus* (range 11000-25000 cells l^{-1}). Some dinoflagellates cells such as *Gymnodium* spp (range 496-2832 cells l^{-1}) were also encountered. Slightly offshore (at Sta. G5) chlorophyll *a* and zeaxanthin concentrations were much lower than those at Sta. G3. Levels of other pigments more or less remained the same. Fucoxanthin and zeaxanthin exhibited a significant decrease from the first observation to the second with a marginal fall thereafter. While peridinin concentrations were higher during SaSu 139, the marker pigments for nanoflagellates were lower during during SaSu 141. The results clearly decay of bloom with time. The lowest concentrations of zeaxanthin were measured at the bottom depths of outermost stations sampled (G9 and G11). Fucoxanthin ranged from 0 to 58 ng l^{-1} with a mean value of 9 ng l^{-1} . Higher concentrations of fucoxanthin generally occurred at Stas. G2 - G6 indicating that the bloom was most intense in the shallow waters. Zeaxanthin had a mean value of 5 ng l^{-1} with a range of 0 -

62 ng l⁻¹, the higher concentrations being generally associated with surface samples collected from stations farthest from the coast (G7-G11) during the decline phase of the bloom. Peridinin, which is often used as a marker pigment of dinoflagellates, also occurred in concentrations ranging from 0 to 18 ng l⁻¹ with a mean value of 6 ng l⁻¹. Nanoflagellate marker pigments were significantly high during the bloom in subsurface waters but showed a gradual decrease later.

The mean value for nanoflagellate pigments was 7 ng l⁻¹ with a range of 0 - 59 ng l⁻¹. In general, concentrations of chlorophyll *a* and other marker pigments varied over large ranges (over two orders of magnitude even after excluding the highest values found at Sta. G3.)

(Insert Figure 2)

3.2 *Changes in chlorinated and brominated halocarbons*

Depth profiles of halocarbons during the initial phase of the bloom are shown in Figure 3 while data from subsequent cruises (SaSu 135, SaSu 139 and SaSu141) are presented in Figures 4-6. The concentrations of all the halocarbons measured were initially high and decreased rapidly with time. However, at Sta. G8 brominated compounds showed a marked increasing trend. Concentration of CHCl₃ ranged from 0.45 - 97.92 ng l⁻¹ whereas that of CCl₄ varied from 0.04 to 3.84 ng l⁻¹ with the high concentrations of CCl₄ being generally associated with high CHCl₃ levels. Both of these compounds were measured in low concentrations during SaSu 135 (0.6 – 17.5 ng l⁻¹ CHCl₃ and 0.02 – 1.13 ng l⁻¹ CCl₄), and the highest value was recorded from surface waters of Sta. G4. Similarly CHCl₃ concentrations during SaSu 139 and SaSu 141 were within the ranges of 0.7 – 25.2 ng l⁻¹ and 0.4 – 35.1 ng l⁻¹, respectively, with the highest concentrations coming from surface waters at Sta. G7 which was also associated with slightly lower temperature (28.5 – 30.2 °C) and lower salinity (35.5 – 35.8). There was a striking similarity in the distribution of CHCl₃ and CCl₄ during SaSu 135 and SaSu 139. Similarly during SaSu 139 and SaSu 141 cruises CCl₄ concentrations were within the ranges of 0.02 – 0.82 and 0.03 – 1.06, respectively with lower concentrations generally occurring in near-bottom waters.

The highest concentrations of brominated methanes (CH₂Br₂ and CHBr₃) were also found during the initial phase of the bloom (Figure 3-7). CH₂Br₂ at the inpatch location had a range of 3.4 – 35.3 ng l⁻¹ whereas during SaSu 135, it had a range of 2.0 - 36.0 ng l⁻¹. Similarly CHBr₃ had a range of 10.7- 16.7 ng l⁻¹ at the inpatch station. Even though station G5 was not under the influence of the bloom CHBr₃ concentrations found here were relatively higher and had a range of 15.0 – 30.4 ng l⁻¹. Brominated methanes (CH₂Br₂ and CHBr₃) also decreased with time. CH₂Br₂ had a range of 1.1 –

37.6 ng l⁻¹ and 2.9 – 23.6 ng l⁻¹ during SaSu 139 and 141 respectively with the highest concentrations being recorded at Stas. G8 and G9 which were under the influence of decaying bloom. The CHBr₃ concentration also showed similar distribution ranging between 1.3 – 16.1 ng l⁻¹ and 2.2 – 9.7 ng l⁻¹ during SaSu 139 and 141, respectively. Interestingly, higher values of brominated methanes were also associated with high zeaxanthin concentrations observed at Stas. G8 and G9.

(Insert Figure 3, 4, 5, 6)

4.0 Discussion

4.1 General characteristic and variability of pigments

Surface water in the study region experience warming between April and May resulting in strong vertical stratification (Figure 2). The resultant restricted supply of nutrients from the thermocline to the surface water leads to oligotrophic conditions. However, even though dissolved inorganic nitrogen concentrations are often below the detection limits, phosphate is never completely depleted. This together with relatively calm weather favours the growth of diazotrophs, especially *Trichodesmium* (Devassy et al., 1978; Sen Gupta and Naqvi, 1984). Microscopic observations confirmed the presence of *Trichodesmium erythraeum* in our area of study and also showed significant bacterial associations with the trichomes. Such associations are well documented (Siddiqui et al., 1992; Villareal, 1992; Nausch, 1996; Mulholland, 2007). We also used phytoplankton pigment data to understand the phytoplankton composition changes during our month-long investigation. In general, Chl *a* biomass was low during the entire period except in waters that were affected by the bloom (see Figs. 4-6). Zeaxanthin was the most abundant marker pigment. The highest concentrations of this pigment were observed in both the surface and subsurface waters at Sta. G8. At this station fucoxanthin and peridinin were also found at shallow depths (14-25 m), suggesting the presence of larger plankton such as diatoms and dinoflagellates (Figs. 4-6). Significantly, fucoxanthin concentrations exhibited a systematic increasing trend with time, especially at Stn G8 that was under the influence of the bloom. This could be related to the release of fixed nitrogen to the water column from the bloom, particularly in its decline phase, which would promote the growth of larger phytoplankton. Such observations have also been reported from Gulf of Mexico (Mulholland et al., 2006). Concentrations of 19' HF and 19' BF pigments were low during our investigation; therefore, much of the fucoxanthin content was presumably from diatoms and not from prymnesiophytes. It would appear that the contribution of nanoflagellates to chlorophyll biomass was mostly from alloxanthin-containing cryptophytes. Diagnostic pigment

indices computed based on Utiz et al. (2006) showed near shore waters to be dominated by microplanktons. In contrast the picoplankton (70-80%) and to lesser extent by nanoplankton (30-20%) dominated the offshore waters. This feature remained consistent during all the three cruises.

4.2 *Halocarbons sources and sinks during the bloom*

Depth profiles of chlorinated halocarbons (Figs. 4-6) suggest strong anthropogenic influence as their distribution was restricted to shallower depths. The strong thermocline which develops during this season inhibits vertical mixing of the water column. Thus, brominated compounds, which have their source in the deeper layers, are vertically restricted. Depth profiles of halocarbons at the bloom station G3 are strikingly different from those at the adjoining Sta. G5 (Fig. 3), with the former showing minor subsurface maxima. Intriguingly, concentrations of chlorinated halocarbons at Sta. G5 were much higher than those at Sta. G3. Halocarbons such as CCl_4 have often been used as a tracer of water masses in the ocean (Krysell, 1992; Krysell et al., 1994; Fogelqvist et al., 1985). It seems reasonable to assume that water masses at the two stations were quite different.

CHBr_3 concentrations recorded at the bloom station G3 was much lower than at other stations. In general, we found that CHBr_3 occurred in lower concentrations relative to CH_2Br_2 . In coastal waters having elevated concentrations of CHBr_3 , the ratio of CH_2Br_2 to CHBr_3 has often been found to be 0.1 or less (Moore and Tokarczyk, 1993; Krysell and Nightingale, 1994; Carpenter et al., 2003; Abrahamsson et al., 2004) while in the open ocean with low CHBr_3 the ratio is much higher (exceeding 0.5 and even 1; Butler et al., 2007, Quack et al., 2007). In the present study, the ratio varied from 0.3 to 0.9 during the first sampling (3rd to 5th April). Thereafter it increased further with time to values exceeding 1. This observation calls for an additional source of CH_2Br_2 , and/or relatively stronger loss of CHBr_3 . Other processes which could also give rise to a high CH_2Br_2 : CHBr_3 ratio have been described in detail by Quack et al. (2007). These workers reported CH_2Br_2 formation by heterotrophic processes in the Mauritanian upwelling system. In addition, biological removal of CHBr_3 by bacteria associated with the trichomes may be an important process that could influence the turnover rate of this compound. Thus, our results are consistent with observations from the Mauritanian upwelling system and highlight multiple sources of CH_2Br_2 formation and/or CHBr_3 degradation by bacteria associated with the trichomes.

Even though there occurred a considerable decrease in halocarbon concentrations during the later phase of the bloom, the average water column concentrations of brominated compounds at Sta. G8 exhibited an increasing trend. This is the same location where the bloom appeared later and could

be observed under various stages of development/degradation during SaSu 135 and SaSu 141. We speculate that brominated compounds could be released from the detrital matter produced by *Trichodesmium*. Recent results of incubations of marine aggregates by Hughes et al. (2008) strongly suggest release of several volatile halocarbons.

One striking observation is the similarity of the distribution patterns of CHCl_3 and CCl_4 . The other noteworthy feature is the high variability in waters affected by the bloom as evident from the spread of values for triplicate samples in the surface layer.

Processes responsible for production of biogenic halocarbons in the marine environment are very complex and are therefore subject of to considerable speculation. Although it is improbable that Chl *a* or other pigments are directly involved in the halocarbon synthesis, they have often been taken as surrogates of processes involved (Schall et al., 1997 and references therein). We performed Pearson correlation analysis between trace gas concentrations, phytoplankton pigments and hydrographic parameters measured during the bloom. The significant relationships obtained are presented in Table 1. CHCl_3 showed strong positive correlation with CCl_4 ($r^2 = 0.94$, $p = 0.05$, $n = 66$). High concentrations of chlorinated halocarbons have been often reported from coastal areas (Nightingale et al., 1995; Christof et al., 2002) and are attributed to production by macroalgae or anthropogenic discharge. The macroalgal growth along the Indian west coast during the SI is negligible, and so the source of chlorinated halocarbons should be mostly anthropogenic. The highest concentrations of the brominated compounds CH_2Br_2 and CHBr_3 were found during the initial phase of the bloom; thereafter the values decreased with time. These compounds also exhibited a different spatial distribution pattern in that they were more concentrated offshore which suggest a strong planktonic source as these stations were away from the mostly-intertidal algal belt where is naturally produced. Also, as pointed out above, there is not much growth of macroalgae during this period. However, significant correlation between any of the marker pigments and brominated compounds was not observed. The chlorinated compounds correlated positively with CHBr_3 , though ($r^2 = 0.76$, $p = 0.05$, $n = 66$). Enhanced concentrations of brominated compounds, especially CHBr_3 , have often been associated with the abundance of diatoms (Klick and Abrahamsson, 1992, Tokarczyk and Moore, 1994; Moore et al., 1996), which in our study were not dominant except at shallower depths. The low correlations could arise from the patchiness of the bloom and/or the presence of high bacterial associations, which could have influenced the turnover rates of these compounds.

Acknowledgement

The authors wish to thank the anonymous reviewer for his valuable suggestions, which has helped in improving the quality of the article. The authors also wish to thank CSIR for support through award of research fellowships/associateships to RR, AP and GN. They gratefully acknowledge the help rendered by the captain and crew of Sagar Shukti at sea. Analyses and visualizations used in this paper were produced with the Giovanni online data system, developed and maintained by the NASA GES DISC. This work forms a part of the CSIR-supported Network Project 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., Loren, A., Wulff, A., Wangberg, A., 2004. Air-sea exchange of halocarbons: the influence of diurnal and regional variations and distribution of pigments. *Deep Sea Research II* 51, 2789-2805.
- Baker, AR., 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.
- Barlow R, Stuart V, Lutz V, Sessions H, Sathyendranath S, Platt T, Kyewalyanga M, Clementson L, Fukasawa M, Watanabe S and Devred E 2007 Seasonal pigment patterns of surface phytoplankton in the subtropical southern hemisphere; *Deep Sea Res PT I* 54: 1687-1703.
- 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.
- Capone, D.G., Subramaniam, A., Montoya, J.P., Voss, M., Humborg, C., Johansen, A.M, Siefert, R.L., Carpenter, E.J., 1998. An extensive bloom of the N₂-fixing cyanobacterium *Trichodesmium erythraeum* in the central Arabian Sea. *Marine Ecology Progress Series* 172, 281-292.
- Carpenter, L.J., Liss, P.S., Penkett, S.A., (2003). Marine organohalogenes in the atmosphere over the Atlantic and Southern Oceans, *Journal of Geophysical Research* 108, D9, ACH 1-1 – ACH 1-13.
- Carpenter, E. J., Subramaniam, A., Capone, D.G., 2004. Biomass and primary productivity of the cyanobacterium *Trichodesmium* spp. in the tropical North Atlantic Ocean. *Deep Sea Research I* 51, 173–203.
- Chameides, W.L., Davis, D.D., 1980. Iodine: Its possible role in tropospheric photochemistry. *Journal of Geophysical Research* 85, 7383-7398.
- Chuck, A. L., Turner, S.M., Liss, P.S., (2005). Oceanic distribution and air-sea fluxes of the biogenic halocarbons in the open ocean. *Journal of Geophysical Research* 110, C10022.

- Christof, O., Seifert, R., Michaelis, W., 2002. Volatile halogenated organic compounds in European estuaries. *Biogeochemistry* 59, 143-160.
- 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.
- Devassy, V.P., Bhattathiri, P.M.A., Qasim, S.Z., 1979. Succession of organism following trichodesmium phenomenon. *Indian journal of Marine Science*, 89-93.
- Dugdale, R.C., Goering, J.J., 1967. Uptake of new and regenerated forms of nitrogen in primary productivity. *Limnology and Oceanography* 121, 196-206.
- Ekdahl, A., Pedersen, M., Abrahamsson, K., 1998. A study of the diurnal variation of biogenic volatile halocarbons. *Marine Chemistry* 63, 1-8.
- Fogelqvist E., 1985. Carbontetrachloride, Tetrachloroethylene, 1, 1, 1-trichloroethane and bromoform in Arctic sea water. *Geophysical Research Letters* 90, 9181-9193.
- Hughes C, Malin G, Turley C, Keely B, Nightingale P, and Liss P 2008 The production of volatile iodocarbons by biogenic marine aggregates; *Limnology Oceanography* 53: 867-872.
- Jeffers, P.M., Ward, L.M., Woytowitch, L.M., Wolfe, N.L., 1989. Homogeneous hydrolysis constant for selected chlorinated methanes, ethanes, ethenes and propanes. *Environmental Science Technology* 23, 965-969.
- Karlsson, A., Auer, N., Bull-Schulz, D., Abrahamsson, K., 2008. Cyanobacterial bloom in Baltic- A source of halocarbons. *Marine Chemistry* 110, 129-139.
- Klick, S., Abrahamsson, K., 1992. Biogenic volatile iodated hydrocarbons in the ocean, *Journal of Geophysical Research* 97, 12683-12687.
- Kononen, K., Leppänen, J-M., 1997. Patchiness, scales and controlling mechanisms of cyanobacterial blooms in the Baltic Sea: Application of a multiscale research strategy. In: *Monitoring algal blooms: New techniques for detecting large-scale environmental change.* (Kahru, M. & Brown, C.W., eds.) Landes Bioscience. Austin, pp. 63-84.
- Krystell, M., (1992). Carbontetrachloride and Methyl chloroform as tracer of deep water formation in the Weddell Sea, Antarctica. *Marine Chemistry* 39.297-310.
- Krystell, 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.
- Krystell, M., Fogelqvist, E., Tanhua, T., 1994. Apparent removal of the transient tracer carbontetrachloride from anoxic sea water. *Geophysical Research Letters* 21, 2511-2514.
- Krishnan, A.A., Krishnakumar, P.K., Rajagopalan, M., 2007. *Trichodesmium erythraeum* (Ehrenberg) bloom along the southwest coast of India and its impact on trace metal concentrations in seawater. *Estuarine Coastal Shelf Science* 71, 641-646.

- Lebour, M., 1978. The Planktonic Diatoms of Northern Seas, Otto Koeltz Science publishers, D-6240 Koenigstein/W- Germany, 244.
- Lovelock J.E., 1975. Natural halocarbons in the air and in the sea. *Nature* 256, 193-194.
- Manley, S.L, Goodwin, K., 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.
- Mills, W.B., Lew, C.S., Loh, J.Y., 1998. Predictions of potential human health and ecological risks from power plant discharges of total residual chlorine and chloroform into the rivers. *Environmental Science Technology* 32, 2162–2171.
- Moore, R. M., and Tokarczyk, R., 1993. Volatile biogenic halocarbons in the northwest Atlantic. *Global Biogeochem Cycles* 7, 195– 210.
- Moore, R.M., Webb, M., Tokarczyk, R., Wever, R., 1996. Bromoperoxidase and Iodoperoxidase enzymes and production of halogenated methanes in marine diatom cultures. *Journal of Geophysical Research* 101, 20899-20908.
- Mulholland, M.R., 2007. The fate of nitrogen fixed by diazotrophs in the ocean. *Biogeoscience* 4, 37-51.
- Mulholland, M.R., Bernhardt, W.P., Heil, A.C., Bronk, A.D., O' Neil, J.M., 2006. Nitrogen fixation and release of fixed nitrogen by *Trichodesmium* Spp in the Gulf of Mexico. *Limnology Oceanography* 51, 1762-1776.
- Nausch, M., 1996. Microbial activities on *Trichodesmium* colonies. *Marine Ecology Progress Series* 141, 173–181.
- Nightingale, P.D., Malin, G., Liss, P.S., 1995. Production of chloroform and other low molecular-weight halocarbons by some species of macroalgae. *Limnology and Oceanography* 40, 680 – 689.
- 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.
- Poulton, A.J., Stinchcombe, M.C., Quartly, G.D., 2009. High numbers of *Trichodesmium* and diazotrophic diatoms in the southwest Indian Ocean. *Geophysical Research Letters* 36, L15610. doi:10.1029/2009GL039719.
- Qasim, S.Z., 1970. Some characteristics of a *Trichodesmium* bloom in the Laccadives, *Deep Sea Research* 17, 555-660.
- Quack, B., Wallace, D.W., 2003. Air-sea flux of bromoform: Controls, rates and implications. *Global Biogeochemical Cycles* 17, 1023.
- Quack, B., Peeken, I., Petrick, G., Nachtigall, K., 2007. Oceanic distribution and source of bromoform and dibromomethane in Mauritanian upwelling. *Journal of Geophysical Research* 112, C10006.
- Roy, R., Prathihary, A., Mangesh, G., Naqvi, S.W.A., 2006. Spatial variation of phytoplankton pigments along the southwest coast of India. *Estuarine Coastal Shelf Science* 69, 189-195.

- Roy, R., 2010. Short-term variability in halocarbons in relation to phytoplankton pigments in coastal waters of the central eastern Arabian Sea. *Estuarine Coastal Shelf Science* 88, 311-321.
- Salawitch, R. J., 2006. Atmospheric chemistry: Biogenic bromine. *Nature* 439, 275-277.
- Scarratt, M.G., Moore, R.M., 1998. Production of methyl bromide and methyl chloride in laboratory cultures of marine phytoplankton II. *Marine Chemistry* 59, 311-320.
- 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 Analytical Chemistry* 359, 298-305.
- SenGupta, R., Naqvi, S.W.A., 1984. Chemical oceanography of the Indian Ocean: north of the equator. *Deep Sea Research A* 31, 671-706.
- Siddiqui, P.J.A., Carpenter, E. J., Bergman, B., 1992. Trichodesmium: ultrastructure and protein localization, p. 9-28. In E. J. Carpenter, D. G. Capone, and J. G. Rueter (ed.), *Marine pelagic cyanobacteria: Trichodesmium and other diazotrophs*. Kluwer Academic Publishers, Dordrecht, the Netherlands.
- Singh, H.B., Salas, L.J., Stiles, R.E., 1983. Selected man-made halogenated chemicals in the air and oceanic environment. *Geophysical Research Letters* 88, 3675-3683.
- Stal, L.J., 2009. Is the distribution of nitrogen-fixing cyanobacteria in the oceans related to temperature?. *Environmental Microbiology* 11, 1632-1645.
- Subrahmanyam, R., 1959. Studies on the phytoplankton of the west coast of India-I and II. *Proceedings of the Indian Academy of Science B*50, 113–252.
- Tomas, C.R. 1996. *Identifying marine phytoplankton*. Academic Press Limited London .pp 857.
- Tokarczyk, R., Moore, R.M., 1994. Production of volatile organohalogens by marine phytoplankton. *Geophysical Research Letters* 21, 285-288.
- Tait, V.K., Moore, R.M., 1995. Methyl chloride (CH₃Cl) production in phytoplankton cultures. *Limnology and Oceanography* 40, 189-195.
- Uitz, Julia., Claustre, Herve., Morel, Andre., Hooker, S.B. 2006. Vertical distribution of phytoplankton communities in open ocean: An Assessment based on surface chlorophyll. *Journal of Geophysical Research* 111, C08005. doi: 10.1029/2005JC003207.
- Villareal, T., 1992. Marine nitrogen-fixing diatom-cyanobacteria symbioses, in *Marine Pelagic Cyanobacteria: Trichodesmium and Other Diazotrophs*, edited by E. J. Carpenter, D. G. Capone, and J. G. Reuter, pp. 163– 175, Kluwer Acad., Dordrecht, Netherlands.
- Vogel, T.M., Criddle, C.S., McCarty, P.M., 1987. Transformation of halogenated aliphatic compounds. *Environmental Science Technology* 21, 722-736.
- Yamamoto, H., Yokouchi, Y., Otsuki, A., Itoh, H., 2001. Depth profiles of volatile halogenated hydrocarbons in seawater in the Bay of Bengal. *Chemosphere* 45, 371-377.

Figure Captions

Figure 1. a) Sampling locations in the eastern Arabian Sea off Goa; b) picture showing patchy *Trichodesmium* bloom observed at CaTS station G3. April.

Figure 2. MODIS satellite observations from (showing the changes in the SST and chlorophyll *a* in the Arabian Sea during the spring intermonsoon season (February-May) of 2007.

Figure 3. Comparison between halocarbons depth profiles observed at CaTS stations G3 (inpatch) and G5 (out patch) n=3 (a-h).

Figure 4. Sampling sections and distribution of halocarbons and phytoplankton pigments in (ng l^{-1}) off Goa during the cruise SaSu 135.

Figure 5. Sampling sections and distribution of halocarbons and phytoplankton pigments in (ng l^{-1}) off Goa during the cruise SaSu 139.

Figure 6. Sampling sections and distribution of halocarbons phytoplankton pigments in (ng l^{-1}) off Goa during the cruise SaSu 141.

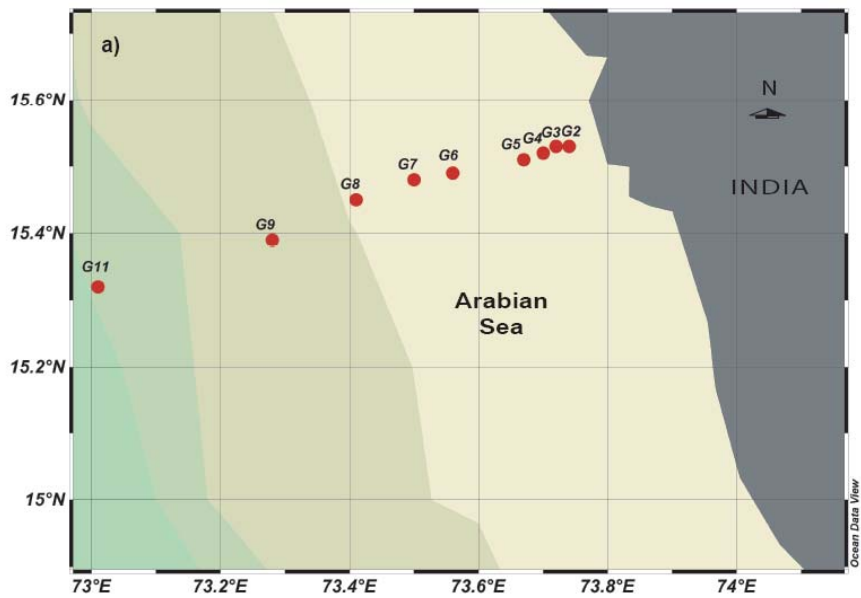


Figure 1

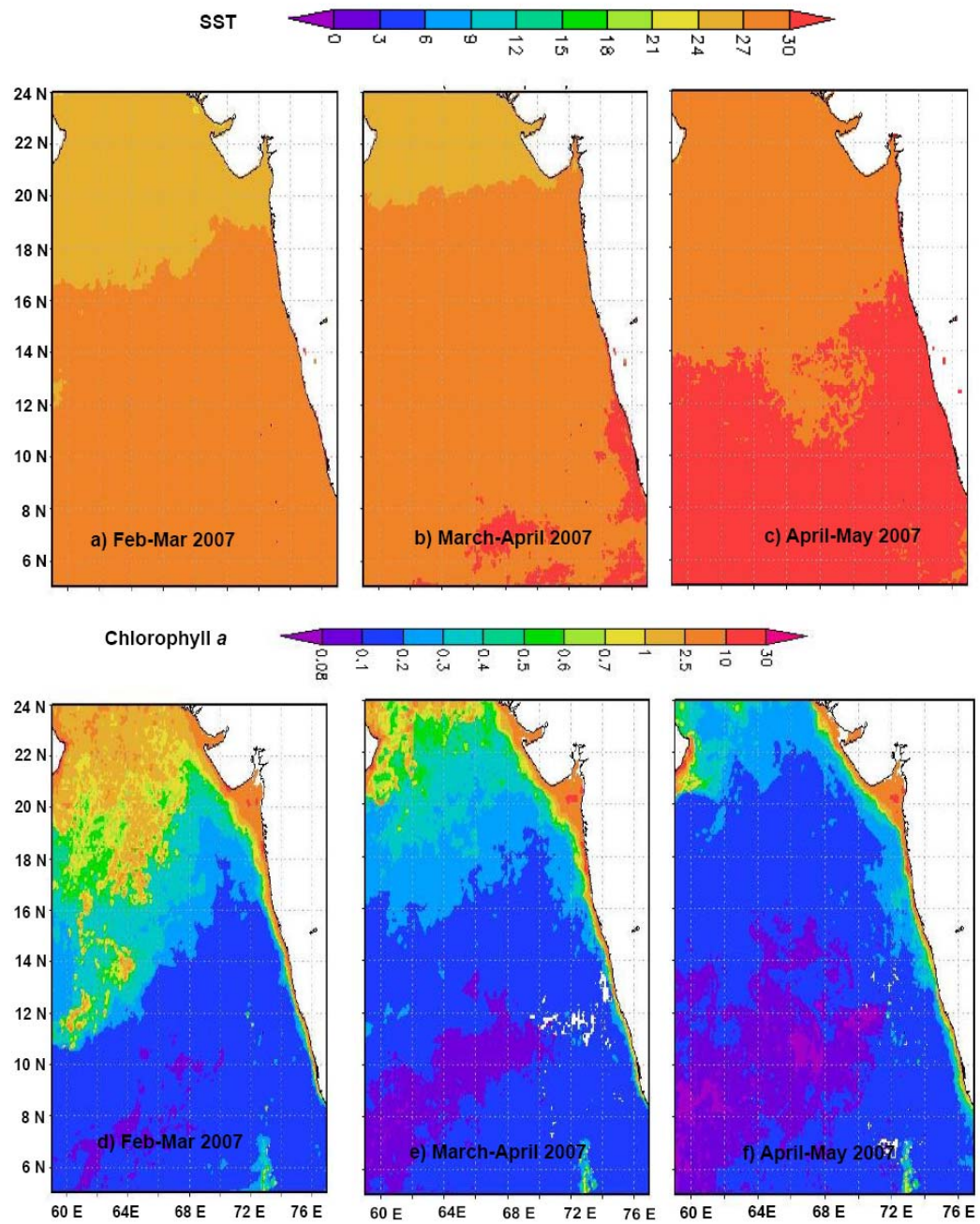


Figure 2

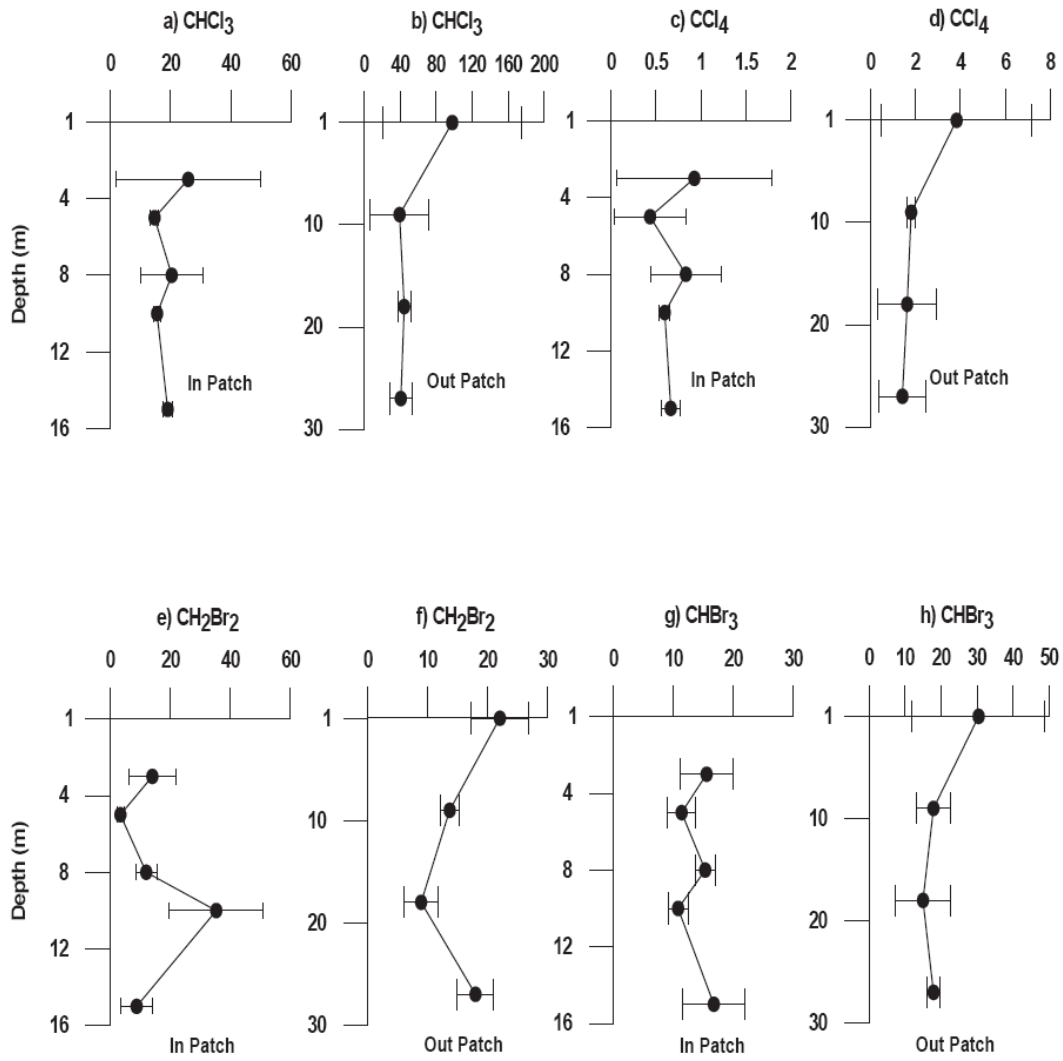


Figure 3

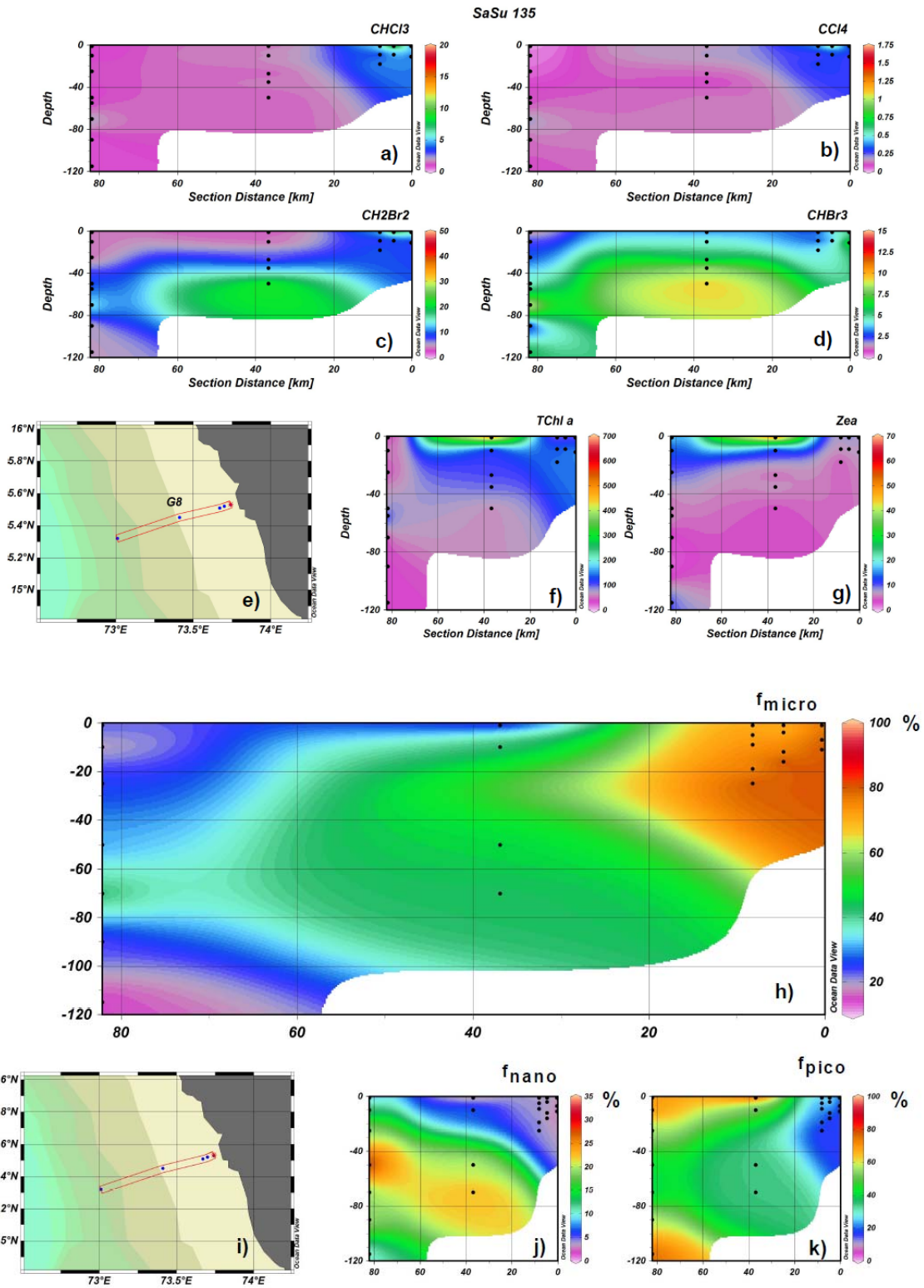


Figure 4

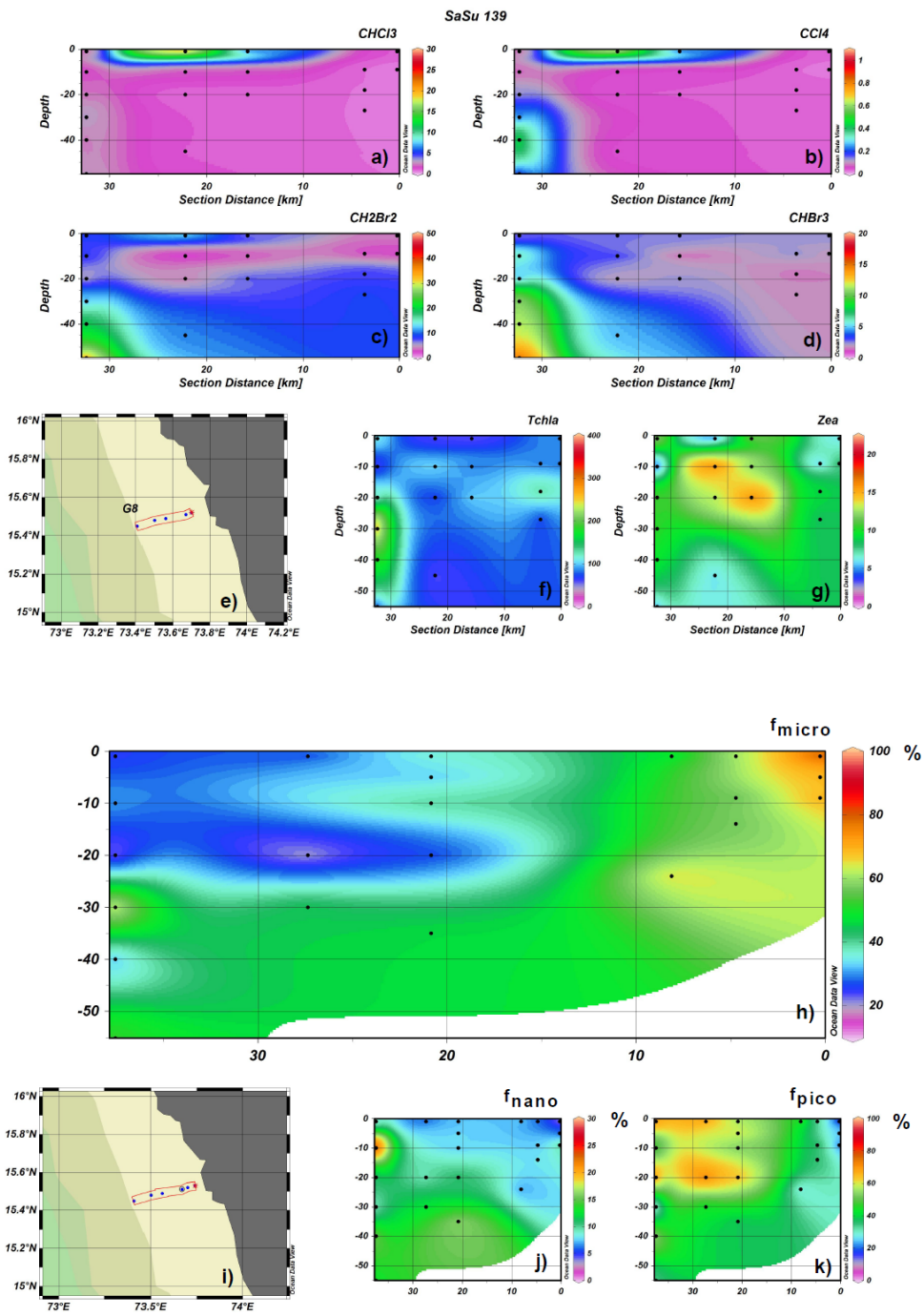


Figure 5

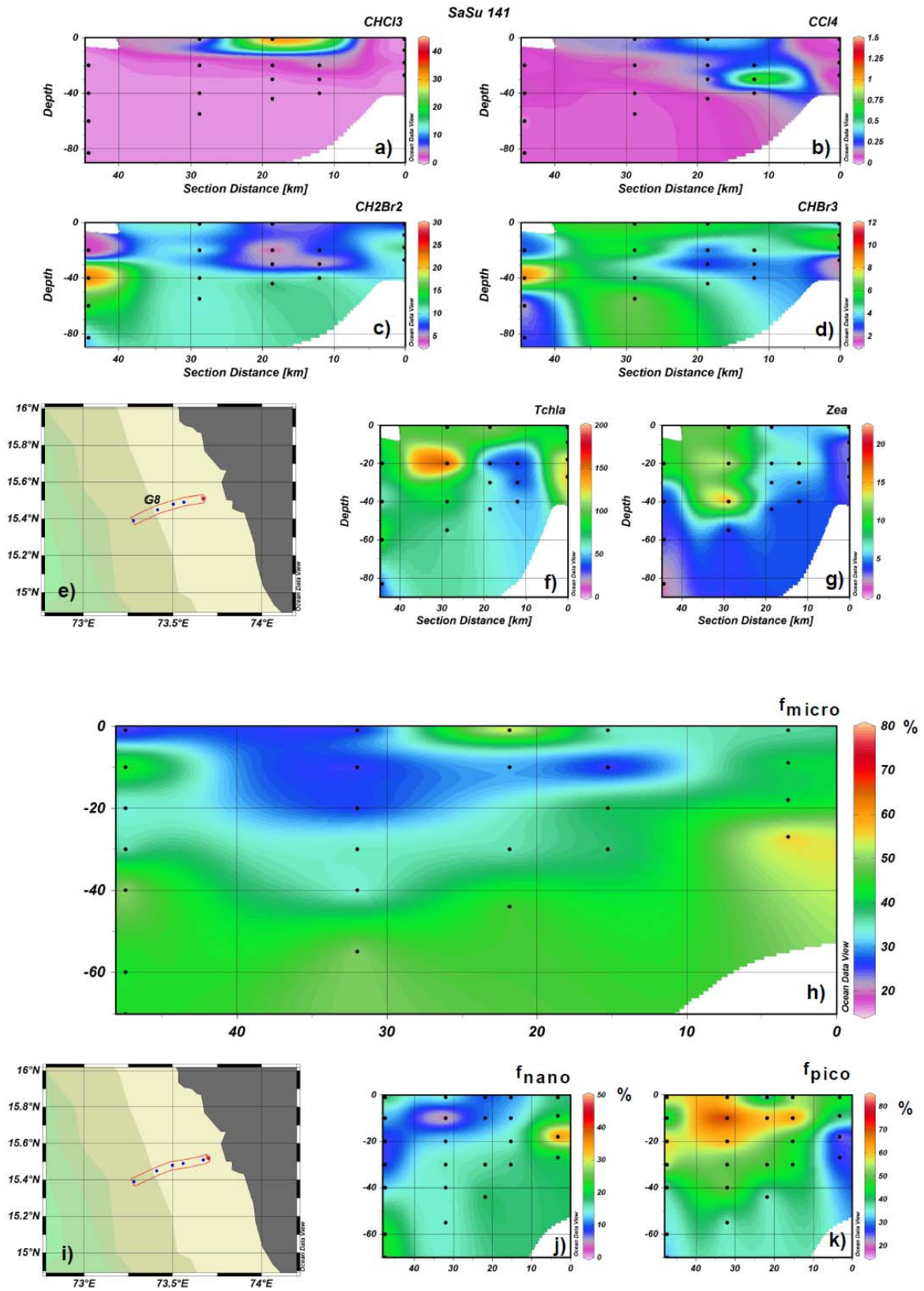


Figure 6

1 **Table I.** Pearson correlations analysis between halocarbons and phytoplankton pigments (n=66). Values in bold are significant at $\alpha=0.05$.

2

| | CHCl ₃ | CCl ₄ | CH ₂ Br ₂ | CHBr ₃ | Temp | Oxy | Sal | Chl a | Zea | Per | Fuco | Allo ³ |
|---------------------------------|-------------------|------------------|---------------------------------|-------------------|---------------|--------------|--------------|--------------|--------|---------------|--------|-------------------|
| CHCl ₃ | 1 | | | | | | | | | | | |
| CCl ₄ | 0.940 | 1 | | | | | | | | | | 4 |
| CH ₂ Br ₂ | 0.257 | 0.285 | 1 | | | | | | | | | 5 |
| CHBr ₃ | 0.764 | 0.764 | 0.324 | 1 | | | | | | | | |
| Temp | 0.081 | 0.058 | 0.147 | 0.031 | 1 | | | | | | | |
| Oxy | 0.079 | 0.079 | 0.157 | 0.032 | 0.483 | 1 | | | | | | |
| Sal | -0.078 | -0.049 | 0.077 | 0.186 | -0.338 | -0.056 | 1 | | | | | |
| Chl a | 0.090 | 0.052 | 0.087 | 0.248 | 0.230 | 0.159 | -0.151 | 1 | | | | |
| Zea | 0.123 | 0.088 | 0.133 | 0.281 | 0.159 | -0.064 | -0.139 | 0.675 | 1 | | | |
| Per | 0.066 | 0.041 | 0.080 | -0.008 | 0.269 | 0.089 | -0.207 | 0.029 | -0.054 | 1 | | |
| Fuco | 0.097 | 0.074 | -0.113 | 0.132 | 0.135 | 0.306 | -0.069 | 0.580 | 0.075 | -0.287 | 1 | |
| Allo | -0.204 | -0.164 | -0.101 | 0.000 | -0.286 | -0.093 | 0.496 | -0.111 | -0.076 | -0.056 | -0.124 | 1 |