CHAPTER 5

IMPACT OF PETROLEUM HYDROCARBONS ON THE COMMUNITY STRUCTURE OF PLANKTON IN THE COASTAL WATERS OF SAURASHTRA

INTRODUCTION

The oceans have been considered as the 'ultimate sink' and have been used as major repositories of anthropogenic waste for decades (Ian, *et al.,* 1993). Wastes discharged or dumped into rivers, estuaries, coastal waters or the atmosphere eventually made their way into the oceans since it was believed that because of its enormous size, the oceans had an infinite capacity to assimilate waste material without any harm to the ecosystem. The coastal ecosystem everywhere in the world is exposed to an ever-increasing environmental impact through increased population, industrialization and tourism. This has required an increased knowledge of the potential effects of these impacts. However, to date there has been very little work done in this geographical area, and the majority of it has been concerned with basic ecological principles rather than effect of specific anthropogenic inputs.

The anthropogens are not layered up in days or month's period, but the years of accumulation of various contagions has increased several folds resulting in an added load on the assimilatory capacity of the ocean. Ultimately, this resulted into localized accumulation of substances with undesirable effect on the ecological balance of the marine ecosystem and thus, endangering its biodiversity. Biodiversity here refers to the plankton communities that are frequently subjected to any adverse variations in water, thus playing a major part in the strategy of the biodiversity conservation. The use of plankton in aquatic ecological research and particularly in evaluating marine pollution is especially effective in long-term changes and detecting input from diffused sources such as petroleum hydrocarbons contamination in seawaters. Hydrocarbon contamination is one contaminant that put world's Oceans in jeopardy. The estimated range of worldwide input of hydrocarbons into the oceans from all sources is 470,000 tones per year to 8,400,000 tones per year. Hydrocarbons, especially oils in the marine waters are found to be present in the concentration detrimental to life (Tang *et al.,* 1997). The amount of pollution by hydrocarbons especially oils may be expected to increase in the near future due to 1. the increase in number of sea going ships, including the tanker fleet, 2. the use of shelf zones for oil drilling and 3. poor international legislative measures to prevent oil pollution in the open seas (Hun and Charles,2000).

According to the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP, 1977) any substance that can cause deleterious effects to human health, hindrance to marine activities including fishing, impairment of quality for use of seawater and reduction of amenities are known as pollutants and the process is referred to as pollution. The most known pollutants or anthropogenic compounds that are carried into the oceans are heavy metals, various pesticides and petroleum products. Amongst all, petroleum hydrocarbons aroused considerable public concern and scientific interest in the recent years as this is responsible for irretrievable damage to the marine life. Under the initiation of Marine Pollution (Petroleum) Monitoring Pilot Project (MAPMOPP) of the Integrated Global Ocean Station System (IGOSS), several studies on the hydrocarbon chemistry in different ocean areas of the world have been carried out (Butler *et al.,* 1973; Wong *et al.,* 1976; Zsolnay, 1977; Levy, 1979, 1980; Suzuoki and Shisakawa, 1979)

Petroleum hydrocarbons are the principle constituent usually exceeding 75% with the other components including sulphur, nitrogen, oxygen and oragnometallic compounds. Depending on the chemical nature of the compounds the hydrocarbons can be divided into four main groups.

a. Normal alkanes, a homologous series from the gas methane to long wax chain.
b. Branched or Isoalkanes – several homologous series, with the isoprenoids being the most important group (e.g. Pristane and Phytane).
c. Cycloalkanes (or naphthalene) dominated by Cyclopentane and Cyclohexane derivates.
d. Aromatic hydrocarbons (and napthenoaromatics) from monocyclic compounds (benzene and its derivatives) to large polynuclear molecule such as pyrene, chrysene, benzopyrene and their derivatives.

The formation of hydrocarbons in nature is a very long and intricate process taking years of compression and heating of the ancient organic materials over the geological time.

According to this theory, the aquatic and terrestrial organisms synthesize hydrocarbon either *de novo* or by conversion from other compounds (such as phytol to pristine) formed by preserved remains of the prehistoric zooplankton and algae, which have been settled in the Sea. The phytoplankton produces normal alkanes in the range n-$C_{15, 17, 19}$ and C_{21} with n-C_{17} usually dominant. Terrestrial organisms on the other hand tend to form coal. The exploration of these hydrocarbon compounds, beneath the Oceans, generally has negative upshots as social and environmental concern. These are mainly caused due to accidents and routine activities such as seismic exploration and drilling. This generates tremendous polluting waste as byproducts. The gallon of hydrocarbon that enters the Oceans each year due to substantiate and unauthenticated reasons has caused detrimental affects on the marine biota (Koshelev, *et al.,* 2005).

Ecologically speaking, all this distress, change the diversity within the organisms thereby brining unprecedented alteration in the community structure of the marine ecosystem. In the present study the marine planktonic ecosystem has been in the focus, as it forms the foundation of almost all organic matter production in the sea, providing the energy basis for the higher tropic levels. The marine planktonic community is a diverse and complex system to investigate and a system for which all mechanism and dynamics are still not fully understood (Verity and Smetacek, 1996). A marine planktonic life can be divided into organisms of varied size groups. Most size groups consist of functional groups of autotrophic phytoplankton and heterotrophic zooplankton. At the base of the planktonic food web is the microbial loop, which consists of bacteria, heterotrophic nanoflagellates and ciliates and which plays a major role in recycling of energy and substrate (Nielsen, 2005), thereby becoming the primary area of concern ones affected by pollutants like petroleum hydrocarbons. Moreover, there are still several areas of major uncertainty regarding the biological effects of petroleum components particularly the chronic sub-lethal effects. Hence, certain important generalizations were made, even if tentative, in the present study. As hydrocarbon, pollution represents a new, adverse, ecological factor, may lead to permanent changes in the biological structure of the Oceans finally reducing their productivity.

FATE OF HYDROCARBONS IN THE SEA

Evaporation: When oil is released on with Ocean surface (e.g. as a slick) it spreads quickly with rapid loss of the more volatile hydrocarbons e.g. low molecular weight compounds known as monoaromatics (Koshelev, *et al.,* 2005).

Dissolution: The hydrocarbons with low molecular weight and degradation products of hydrocarbons with large molecules are more polar in nature, thus have a greater solubility in water. This leads to more toxic compounds to be dispersed preferentially. This suggests that with an area of good dispersion there is a rapid decrease in distribution of marine life (Koshelev, *et al.,* 2005).

Adsorption: A major path for many hydrocarbons into the marine system is adsorption and absorption of particulate matter. Hydrocarbons may enter the sea already associated with such particulate matter or this may occur in the water column with hydrocarbons originally in a free or dissolved phase. In the areas of little water movement, such hydrocarbon particulate may sink rapidly and reach the sediment or may be consumed by particulate–feeding biota (e.g. Zooplankton or benthic macrofauna). By and large, the hydrocarbons may enter the tissues of biota, may get metabolized or may be discarded *via* the faeces or pseudofaeces (Koshelev, *et al.,* 2005).

HYDROCARBONS IN MARINE BIOTA

With continued development of petroleum reserves there has been growing interest in the fate and effects of petroleum hydrocarbons that may be spilled in marine waters. There have been a quite a few studies made during the past decade on the ecological effects of hydrocarbons spillages in the Indian coastal waters.

Generally speaking, the diverse habit and habitat of most of the marine flora and fauna make them exceedingly vulnerable to both acute and chronic exposure to environmental contaminants such as petroleum hydrocarbons (Fossato and Canzoneir, 1976; Teal and Farrignton, 1977). There are number of pathways for input of hydrocarbons and most of these may be considered to cause gradual change to the environment which is not immediately obvious (Chripps and Priddle, 1991). Studies identifying pollution as an exogenous source of hydrocarbons for marine animals have been made by Ehrhardt (1972) using oysters from Galveston Bay, Texas; by Morris (1973) using barnacles (*Lepas fascicularis)* caught from Australian waters close to refineries.

The hydrocarbons (PHCs) released in to waters are not a single constituent but a complex mixtures of thousands of organic compounds, with different characteristics. Hence, their effect on marine biota varied with the characteristics of the compounds. Once released into the environment all these compounds spread at an alarming rate, and are subjected to continuous change due to bacterial degradation and photo oxidation processes. The accumulated hydrocarbons may act as internal photoreceptors, causing photo oxidation in the tissues as reported by Thomas, (2004) in copepods. The observed sensitivity to photo enhanced oil toxicity may have further implications since copepods might transfer hydrocarbons to other trophic levels. Further, in an effort to reduce the risk of the loss of the marine biodiversity after an accidental spillage of oil in the marine ecosystem, chemical dispersing agents are employed to increases the functional solubility of many of these compounds. However, in the process of dispersion, increased concentration of these compounds move into the water column, possibly enhancing its bioavailability to the marine organisms (Nayar, *et al.*, 2004).

The organisms such as phytoplankton excessively take up the active ingredient like phosphates from the dispersing agents and thereby lead to eutrophication and further influencing the higher trophic levels of the food chain. Moreover, the petroleum hydrocarbons may also have less obvious but serious long term repercussions, such as detrimental affects on the planktonic phases of many of the marine organisms. It is likely that, such ill-fated incidents of oil spillage in the Seawaters have the potential to cause immense damage, particularly to the intertidal and sub tidal ecosystem such as coral reefs, mangroves and sea grass communities and so on (Imma, *et al.*, 2005)

To further, comprehend, the various radical consequences of the petroleum hydrocarbons spillage and its repercussion on the existing community, several seminars were conducted at different parts of the world. This reveals the effects of hydrocarbons on marine ecosystem that are responsible for altering its ecology and biodiversity (Johnston and McIntyre, 1976). The current situations all over the world are bothersome, in view of its apparent degradation of plankton community, accompanied by shift in compositions and domination of monospecific species of zooplankton and phytoplankton in marine ecosystem. In spite of significant efforts by national and international researchers (UNESCO, 1988; Cattaine and Coini, 1992 and Dalla Venezia, 1996), a definite holistic evaluation of the real ecological status of the plant community due to anthropogenic impact through hydrocarbon pollution yet remains insufficient.

Back home, India is no exception, with a huge infrastructure in petroleum industries and being acknowledged for having the second largest ship-breaking yard in the world the impact of PHCs on the marine biota is hardly gain any concern. Hydrocarbon pollution especially oil is considered to be a major pollutant in the Indian waters and falls in the top category of pollutant as classified by the United Nations Environment Programmers. Gujarat state is not exempted, with all flourishing Petroleum industries e.g. ONGC, Hindustan Petroleum and Reliance petrochemical industries etc indeed have radically affected the hydro-physical, hydro-chemical and hydro-biological parameters of the Seawater in the state. Since the living resources of the oceans and seas have been the target for exploitations in various episodes extending back to over two centuries (Everson, 1987). The three study stations of the Saurashtra have been exploited for the same motives. Ships breaking, substantial fishing fleets and tourisms were the major cause of hydrocarbon release in the coastal regions of Saurashtra.

A hydrocarbon compound that enters the marine environment affects a number of abiotic factors as well as the physical and chemical properties of the compound itself. The plankton may be at greater risk than the other biotic components of the marine ecosystem, due to the proximity to hydrocarbon compounds floating on the sea surface and their general sensitivity to the toxic components in the hydrocarbons. For these minute organisms floating or swimming in the top few centimeters of the surface film of the Sea water (e.g. neuston) the impact may be greatest of all (Clark, 1989). Although, the hydrocarbon compounds adversely affect phytoplankton populations, their patchy distributions and high rate of proliferations can nullify the overall impact (Neff, 1979). Thus, phytoplankton population recovers quickly, and returns to the population levels existed prior to hydrocarbon pollution. Depending on petroleum hydrocarbon concentration, photosynthesis by algae is also either enhanced or reduced as evidenced by the work on algal cultures (Goutx, *et al.,* 1984). However, among the holoplanktons of marine ecosystem, copepods have been the target of much research regarding the effects of petroleum hydrocarbon contaminations. Zooplankton accumulates significant amounts of Petroleum hydrocarbon *via* ingestion of oil, causing augmentation of substance in the tissues of these organisms leading to bioaccumulation which is evident from observations made on zooplankton following major spills at sea (Thomas, 2004). Consequently, the effects of hydrocarbon are not only constrained to plankton alone, but nektons, marine as well as coastal birds and mammals are also found susceptible to hazardous effects of hydrocarbon contamination in marine ecosystem. Ironically, the hydrocarbon also induced acute damage to corals that may result in a collapse of the complex community of the organisms, which live in close association with the corals (Loya and Rinkevich, 1980)

Collectively saying, increased hydrocarbon pollution in the last few years seems to be connected with the fundamental economic and social changes all over the globe. Hence, it has become a major issue of concern irrespective of the causes. Thus, a systematic long term study, in a regional context, and their effects on biota is necessary to be instigated before irreversible damage prevail. Regrettably, the problem of hydrocarbon pollution in Gujarat state has not received considerable scientific attention despite its possible severity on the marine biota. Hence, taking in to account the deleterious effects of hydrocarbons to specific biological components of the ecosystem, the **objective of this chapter was set to evaluate the effect of anthropogenic activities especially petroleum hydrocarbons on the community structure of plankton in the coastal waters of Saurashtra.**

MATERIALS AND METHODS

SAMPLE COLLECTION AND ANALYSIS

The quantitative study was performed for establishing the significant damage caused by hydrocarbons to plankton community structure prevailing in the study stations located at the Gulf of Cambay and the open coast of the Arabian Sea. The samples were collected and analyzed according to 'Standard Methods for the Examination of Water and Waste Water' (AWWA and APHA, 1998). The detailed procedure is described elsewhere (Chapter 2).

STATISTICAL ANALYSIS

Prior to statistical analysis, all variables were tested for homogeneity by comparing means. After asserting the normality of the data for all variables, Independent group Analysis of Variance (One Way ANOVA) was performed to test the difference between the means for all the parameters. The statistical analyses were done using the programme Origin Ver. 7.

RESULTS

SEASONAL CONCENTRATION OF PETROLEUM HYDROCARBON AND BIOLOGICAL OXYGEN DEMAND

Seasonal changes in the levels of petroleum hydrocarbons (PHCs) and biological oxygen demand (BOD) are expressed as mean and standard error values as shown in Table5.1.

DIU

The seasonal fluctuations in the petroleum hydrocarbon at all the stations were observed. The sampling site Diu, showed reasonably low concentration of PHCs values than the other two stations i.e. Veraval and Alang. The minimum concentration recorded in Diu was 22.08 mg/L in post monsoon. The maximum concentration of 26.5 mg/L was observed during pre monsoon. The winter and monsoon reflected almost similar values of hydrocarbon concentration for reasons unknown. The BOD also showed a similar trend with the maximum value of 2.63mg/L during pre monsoon. The lowest value of 1.28 mg/L was witnessed during in the post monsoon season. The BOD increased in monsoon, with a fall in winter (Table 5.1 and Figure 5.1.1).

VERAVAL

The PHCs concentration values in Veraval remained more or less similar during pre monsoon and monsoon seasons of the year. The winter and post monsoon season were characterized by a descending trend in hydrocarbon concentration. An increase in the level of BOD was observed during monsoon. The BOD showed a definite decrease from 3.68 in winter to 2.87 mg/L in post monsoon, while the lowest value was recorded during pre monsoon season (Table 5.1 and Figure 5.1.2).

ALANG

The levels of biological oxygen demand and PHCs fluctuated significantly during different seasons in Alang. The Petroleum hydrocarbons varied from a minimum concentration of 26.2mg/L in monsoon to a maximum of 29.4 mg/L during pre monsoon season. More or less similar concentration of petroleum hydrocarbons were documented during winter and post monsoon. A film of petroleum was visibly evident covering some stretches of the coastal waters of Alang. The BOD levels also followed the same trend as that of PHCs. As with an increase in PHCs content during pre monsoon, there is a concomitant rise in BOD up to 4.73mg/L. The minimum concentration of 3.45mg/L was observed during the post monsoon, however monsoon encountered the maximum BOD value, though the petroleum hydrocarbon showed less concentration. Since, many other biologically degradable organic matters may be washed into the Sea; it has direct influence on the dissolved oxygen contents in water, thereby increasing the BOD level of coastal water (Table 5.1 and Figure 5.1.3)

HYDROCARBONS AND PLANKTON COMMUNITY

Although the seasonal changes in phytoplankton and zooplankton population in response to PHCs in all the three stations *viz* Diu, Veraval and Alang were clearly evident, equally noticeable was their regional difference. In order to understand whether the values differed significantly in relation to various seasons and stations, one way ANOVA was carried out. Mean comparison of biological component with PHCs and BOD using Tukey's test was performed for all the three stations (Table 5.2). The results in the table shows that the mean values of zooplankton and phytoplankton population with that of PHCs were significantly different at 0.05 levels of p value at Alang, while the difference was not significant at the other two stations *viz* Diu and Veraval. Response of the plankton community and its diversity towards the petroleum fractions were similar, though differing in intensity at all the three stations. Phytoplankton density at all the three stations showed a decline in pre monsoon season. This may be due to some pertinent reasons like variations in the physicochemical parameters including nutrients or the presence of some anthropogenes in seawaters. Toxicity of these compounds to plankton and other marine inhabitants cannot be overruled.

The annual diversity value for plankton was found maximum at Diu with the diatoms dominated over the dinoflagellates suggesting a greater tolerance of diatoms to PHCs contents in the seawater. This was followed by Veraval. However, Alang exhibited a low diversity of phytoplankton with elevated hydrocarbon contents from its ship breaking activities along with heavy loads of sewage as well as other inorganic wastes. This principally helps to sustain centric diatoms like *Thalassiosira* and *Coscinodiscus sp.* Furthermore, the graphical representation illustrates that zooplankton diversity has not respond to increase in petroleum hydrocarbon, in Diu, even with significant increase in hydrocarbon concentration in pre monsoon, the site showed greater diversity. The overall zooplankton diversity showed similar values. However, the phytoplankton diversity seemed to be affected by the concentration variation, as the diversity dropped with increase in concentration of hydrocarbons during pre monsoon. There occurred a virtual increase in diversity when a drop in the hydrocarbon values was substantiated during the rainy season and post monsoon seasons (Figure 5.2.1and 5.3.1).

In Veraval, zooplankton diversity seems to be influenced by the hydrocarbons in the water. The zooplankton diversity showed a direct relationship as the diversity dropped with increases in PHCs level during pre monsoon and monsoon season. After the spell of rain, a slight gain in its diversity, with a fall in hydrocarbon concentration was apparent. Nevertheless, a reverse trend was observed during winter wherein a hike in hydrocarbon concentration with a concomitant increase in zooplankton diversity was observed. This might be due to the presence of tolerant species of zooplankton. The impact of hydrocarbons on phytoplankton diversity indicated inverse relation. The decrease in hydrocarbons after rains indicated an increase in phytoplankton diversity. However, winter, summer and rainy season encountered a drop in the phytoplankton density and diversity with a raise in concentration of PHCs in the water (Figure 5.2.2 and 5.3.2).

The phytoplankton cells at Alang, showed considerable reduction in pre monsoon season with an attendant increase in the PHCs value. This increase in PHCs probably could be due to substantial changes in the abiotic factors like temperature, oxygen content and presence of other anthropogenic activities (Arturo and Mingjie, Unpublished). In general, the petroleum hydrocarbon can inhibit the growth of both phytoplankton and zooplankton, and can restrain the growth of other flora and fauna as well (Chen 1998). The figure 5.2.3 and 5.3.3 relates to effects of hydrocarbons on the phytoplankton and zooplankton diversity and shows concomitant variation in the PHCs concentrations at all the three seasons except in winter. In winter, maximum zooplankton diversity was observed, even though the hydrocarbons were high in the water. The probable reason could the high nitrate levels (total oxidized nitrogen) observed during winter at Alang. The zooplankton diversity dropped with a maximum increase in hydrocarbon concentration during summer. The phytoplankton exhibited a sharp increase in diversity with a drop in hydrocarbon concentration during monsoon and post monsoon. Nonetheless, the maximum fall in the phytoplankton diversity was recorded during the pre monsoon season.

The results of one way ANOVA give credence for the inflictions of PHCs on the plankton community, the plankton diversity indicated significant relation ($P<0.05$) with hydrocarbon contamination at Alang. Nevertheless, this can not be attributed to single reason like the presence of hydrocarbon alone, as coastal waters of Alang contain many anthropogens dissolved/dispersed in its water column. However, no such relation was observed for Diu and Veraval (Table 5.2).

Thus, it explains the different response in varied environmental conditions for the effects of the same contagion e.g. PHCs. The zooplankton, which are rather most sensitive to petroleum hydrocarbons in seawaters were high in numbers. Numerical abundance showed that Bivalves 3.3 % and Chetognaths 33.16 % formed a bulk in Alang. The Chetognaths have been reported to be successfully thriving in the Alang waters in spite of increase in PHCs content. Whereas in Veraval and Diu copepods were reported to be a major groups indicating less stress of various anthropogenic compounds including PHCs in the seawaters. Whereas, the phytoplankton population at all the three stations showed considerable increase except for Diu. This rise in population may be due to the increase in the diatom population and to some extent inhibition in the growth of the dinoflagellates. This is of course, only a single comparison, from which a general conclusion is difficult to make, but it illustrates the point that there can be major difference between the responses of different communities to same pollutant in an ecosystem.

DISCUSSION

The hydrocarbon pollution should be considered not only with a view to understand its short-term effect but chronic effects also need to be evaluated. However, little attention has been given to what happens with the hydrocarbons once it is out of sight (Murphy, 1971). Blumer *et al.* (1971) pointed out, as did many other scientists, that although major catastrophes such as the wreck of a tanker make headlines, the smaller day to day spills or discharges in coastal waters produce chronic pollution that is much larger in total volume and more severe in biological consequence are largely neglected. Long after visible traces of oil disappeared from the sea (Blumer *et al.,* 1971), various hydrocarbon fractions remained present at sizeable depth (Blumer *et al.,* 1971; Blumer and Sass, 1972). The community structure and species abundances of marine organisms may change for long periods of time following a single oil spill and perhaps even more so in areas subjected to chronic hydrocarbon pollution. The dissolved hydrocarbon causes contamination of seawaters that in turn result in changes to the composition of plankton communities living in and on the waters and sediments. This hydrocarbon contagion significantly affects the plankton communities with response which is highly complex and perilous.

Many investigators stressed on the need for the baseline biological studies in regions with high probability of future subjection to pollution, leading to better evaluation and quantification of its long term effects on animal and plant communities (Mitchell *et al.*, 1970; Birkeland *et al.,* 1976; Stirling, 1977). In the present study, compartmentalization of the species was a unique feature noted from all the three sampling stations. To be more precise, few specific species were exclusively found in these study stations. Therefore, it can be concluded that compartmentalization of species in community composition is evaluation of long-term effect in response of some of the anthropogenic compounds present in marine waters. The degree to which petroleum hydrocarbons influence the plankton population varies with concentration, type of compound and also with species having different sensitivity to the hydrocarbons present in the seawaters.

The increased hydrocarbon content in the tropical marine environment has caused many negative effects to the residing communities. Present observations suggest that among all the three study stations, Alang, the largest ship breaking yard, is considered as the major dump yard for all the anthropogenic waste. The main pollutants of the ship scrapping industry and its associated wastes at Alang are heavy metals, petroleum hydrocarbon and bacterial contamination. There also occurred a visible sheen of oil on water surface, suggesting that petroleum inputs are derived from the external activities like ship breaking and removal of the ballast, and there by oil residues are washed into the sea. The coastal waters of the other two stations Veraval and Diu also showed reasonable amount of pollutants as nutrients, trace metals and dissolved/dispersed PHCs. The influences of other factors, if any, prevailing in the study stations cannot be explained at present. Yet the levels of hydrocarbon content along the Gujarat coast are comparatively lower than those reported from Maharashtra coast (100mg/L; Mehta *et al.,* 1984) and from the Madras harbor (11-139mg/L; Selvaraj *et al.*,1999).

Scores of studies on algal species and specific pollutants have been published. Most have described effects upon population growth or photosynthesis and indicate that, generally, phytoplanktons are as sensitive to pollutants as zooplankton. During the present study, a remarkable increase in PHCs values was observed during the pre monsoon season at all the three stations, with Alang recorded the maximum concentration. This impact was prominently seen as the significant level using ANOVA. The pre monsoon relatively represented the lowest phytoplankton and zooplankton density at all the three stations. The reasons endorsed were for the presence of hydrocarbons and some other harmful contagions in water that may interfere with the Hill reaction of photosynthesis especially in the case of phytoplankton in the water. The Hill reaction is a light dependent transfer of electrons from cell water to nictotinamide dinuleotide adenine phosphate (NADP) and is inhabited by presence of such compound as PHCs in water. However, the observations of Srinivas *et al.* (2005) for the seasonal variations in PHCs concentrations were contradictory stating that, the concentrations of petroleum hydrocarbons and heavy metals were higher in winter than in monsoon and summer. They suggested, the concentrations of total PHCs and PAHs are about three times higher in the winter and two times in the monsoon or summer at Alang–Sosiyo and about twice in all the other seasons.

Hydrocarbons may also affect species composition in a community. Eutrophic systems commonly contain blue-green algae (Cyanophyta), especially in summer (Walsh, 1975). Such seasonal variations were evident in phytoplankton and zooplankton population in the present study and their regional difference also appears to be equally conspicuous. Varying sensitivities to pollutants among zooplankton species could cause changes in community structure by affecting variables such as rate of increase, rate of predation, mortality and population density. The situation was demonstrated by Sprules (1975) who reported major changes in composition of crustacean zooplankton communities from highly stressed salt water lakes. The zooplankton population is a function of the intrinsic rate of increases, natural mortality, mortality due to pollution, and rate of predation. In the present study, higher concentration of PHCs in the coastal waters seems to impart its adverse affect on growth of the phytoplankton and zooplankton population as evidenced from the observed low diversity values at Veraval and Alang. The degree to which hydrocarbons influence plankton varies with concentration, compound and type of species (Verleckar *et al.*, 2006).

In city like Alang where ship breaking activities are performed at a very large scale, single factor can not be considered as the cause of ecological damage, various refuse and disposal materials are also discharged and spilled from the scrapped ships that gets mixed with sediments at the coast and finally gets washed into the waters creating a menace. The other two stations Diu and Veraval also provide a clear indication of the seriousness of the impacts of multifarious compounds in plankton population. However, Batten *et al.* (1998) suggested a paradoxical statement based on the oil spillage in the Southern Irish Sea, indicating that the petroleum hydrocarbons might not reduce the growth of phytoplankton or zooplankton. The spillage of fuel and crude oil induced no deleterious effect on the community composition of either phytoplankton or zooplankton. This provides an insight that, hydrocarbon alone may not be acting as a causative agent for brining any variability in plankton population. Besides, some of the sturdy forms e.g. *Cocinodiscus, Rhizosolenia* and *Thalassiosira* had proliferated well and retained in high numbers. This could be attributed to the presence of nutrients like nitrates and phosphates present in the dispersants or the sewage along with PHCs in the coastal waters.

Whatever the extent of damage, the reproductive success of the tolerant survivors, as well as the influx of eggs, juveniles and adults of these tolerant ones underpins the recovery process. In the present study some of the tolerant species like *Bivales, Sagitta enflăta* and *Sagitta* were seen at the coastal waters of Alang. In Veraval, *Foraminiferans and Gastropods* were abundantly proliferated. *Amphipoda* and other sensitive taxa however, were absent. The reason authorized for the low copepod population in Veraval, being the largest fish-landing center of Gujarat, is that it contains unreasonable amount of organic waste along with oil pollution from the small ships and boats. Reports indicate that copepods are sensitive to mixtures of different types of pollutants (Ramaiah and Nair, 1997; Gajbhiye *et al.,* 1995). Uye (1994) has also reported reduction in copepods due to excessive release of nutrients in the coastal waters. Therefore, conclusions can be drawn that the coastal areas; Alang-Sosiya ship breaking yard and fish landing area like Veraval are receiving large quantities of industrial wastes, sewage effluents and hydrocarbons from many unscrupulous sources.

Providentially, the topographical features of Alang allow excellent mixing and flushing conditions of water during high tide in its coast. The wind induced coastal currents in Alang also keeps this water well aerated thereby retaining enough oxygen and moderate BOD levels except during some seasons. These conditions are helpful in brining dispersion of organics and other pollutants thereby reducing the severe pollution stress as one expected. Hence, certain species of phytoplankton and zooplankton proliferate well in such waters. This could be further used as a measure to detect environmental disturbances prevailing at Alang. Lower species diversity and propagation of certain species of phytoplankton have been used as markers for some ecological disturbance caused due to anthropogenic compounds prevailing at Kulai regions of Karnataka coast (Samyda, 1963) cited by (Tiwari *et al.*, 1998). The Diu, which indicates less contaminated water and fairly stress free conditions of water, abode high diversity of flora and fauna. This implies an improved quality of the water and prevalence of a healthy community.

The other factor that contributes significantly to the variations in a marine ecosystem is the tidal influx. The hydrocarbons dissolved or dispersed in water due to tidal influx can easily reach out to the most delicate flora and fauna of the marine ecosystem. The information about the effects of oil on plankton is much sparser than for the littoral and benthic organisms. Generally, plankton is thought to remain rather unaffected by oil, mainly for its capability to escape the contaminated area of the water. This is partially true for larger zooplankton and in case of small scale hydrocarbon pollution in seawaters. Further, oil is reported to affect the seashores and bottoms more rather than the open water ecosystems (Robertson, 1998).

The open waters of the ocean and the associated pelagic and sea bed communities have shown fewer impacts from petroleum hydrocarbon contamination. The high dilution potential that the marine habitat provides is a major mitigating factor (Ratna Bharathi *et al.*, 2001). Even through the laboratory research has shown that planktonic organisms which live in surface waters can be variously affected by hydrocarbons in water, no long term effects have been demonstrated due to their huge regenerative potential, as well as immigration from outside the affected area. This regenerative potential is fundamental to the important role the plankton plays in the food chains of the world's oceans and seas.

Nonetheless, concerns are often expressed about the effects of spills on fish and shellfish eggs and larvae which are found in the plankton; especially as their sensitivity to oil pollution has demonstrated in laboratory toxicity test. However, there is no definitive evidence that oil induced mortalities of fish and shell fish eggs and larvae in the open sea have resulted in any significant effects on the future of adult populations. This is not surprising because oil induced mortalities of eggs or young life stages are often of little significance compared to huge natural losses happen each year through predation, temperature changes and storms.

Probably the most vulnerable of the organisms which use open waters are sea birds which are easily harmed or killed by floating slicks. Although the oil ingested during preening may be lethal, the most common form of death is from drowning, starvation and loss of body heat following damage to plumage due to oil. Nevertheless, research has rarely shown any detectable impact form spills on breeding population, even when mortalities from hydrocarbon contamination are known to have been high.

Against this background it is inevitably difficult to establish the precise extent and likely duration of environmental damage caused by hydrocarbon contamination and to distinguish the changes brought about by a variety of other factors both natural (e.g. climatic and hydrographic) and man made (e.g. commercial fishing or other industrial pollution). The environment impact of hydrocarbon has been extensively researched over the past for few years and more have been learnt about the nature and duration of such effects on the marine ecosystem. The one thing that really made one to deem is the recovery of the damaged habitats and species.

It can be concluded from the above discussion that the petroleum hydrocarbons affect the marine organisms in a variety of ways, ranging from death to biomolecular, pathological and cellular effects. The effect on various aquatic organisms including plankton, whether reversible or not, is depends on numerous physical and biological factors. Apart from the ecological response, the apparent complexity of the metabolic response to petroleum is hardly surprising in view of the broad range of physiologically active compounds present in the hydrocarbons and the physiological processes that are undoubtedly affected in different aquatic species. An evaluation of the consequences of the environmental contamination requires understanding of the extent to which it is responsible for changes in individuals and populations in the affected area (discussed in depth by e.g. Clark 1982, Jones 1982).

The results of these studies do not completely extrapolate the absolute conditions on the various affects of hydrocarbons on the plankton population or in general to a complete aquatic ecosystem. This also helps in understanding that, once the PHCs enters into the aquatic medium, they persists for longer periods of time in the ecosystem. Some forms of the biota in the ecosystem have varying degrees of tolerance or sensitivity towards petroleum hydrocarbons with some population being destroyed by the hydrocarbon contents in the seawater. Nevertheless, some of the populations in the biota may withstand the new challenges in the surrounding environment and flourish. The recovery and return of the pristine quality of the coastal waters in this location might take a prolonged period. It is likely that more studies are needed to understand and identify the long term consequences of the anthropogens including petroleum hydrocarbons on the aquatic biodiversity and methods for enhancing its recovery.

Table 5.1. Petroleum hydrocarbons (PHCs) and Biochemical Oxygen Demand (BOD) values during different seasons at three stations *viz* Diu, Veraval and Alang.

PHCs mg/L

Seasons	Diu	Veraval	Alang
Winter	24.12 ± 1.07[@]	27.25 ± 0.48	27.79 ± 0.87
Premonsoon	26 .42± 0.80	28.05 ± 1.04	29.40 ± 0.60
Monsoon	24.82 ± 0.82	28.2 ± 0.82	26.21 ± 0.40
Postmonsoon	22.08 ± 1.05	24.02 ± 0.05	27.24 ± 0.71

BOD mg/L

Seasons	Diu	Veraval	Alang
Winter	1.59 ± 0.06[@]	3.68 ± 0.21	4.07 ± 0.04
Premonsoon	2.63 ± 0.08	2.49 ± 0.03	4.73 ± 0.75
Monsoon	1.86 ± 0.05	4.75 ± 0.09	5.90 ± 0.58
Postmonsoon	1.28 ± 0.05	2.87 ± 0.11	3.45 ± 0.23

[@] Values are expressed as mean ± SE; n = 3

Table 5.2. Results of one-way analysis of variance (ANOVA) followed by Tukey's honest significant difference (HSD) tests between chemical variables (PHCs/BOD) and biological variables (phyto/zooplankton diversity).

DIU

Parameters	Phytoplankton Diversity	Zooplankton Diversity
PHCs	NS	NS
BOD	NS	NS

VERAVAL

Parameters	Phytoplankton Diversity	Zooplankton Diversity
PHCs	NS	NS
BOD	NS	NS

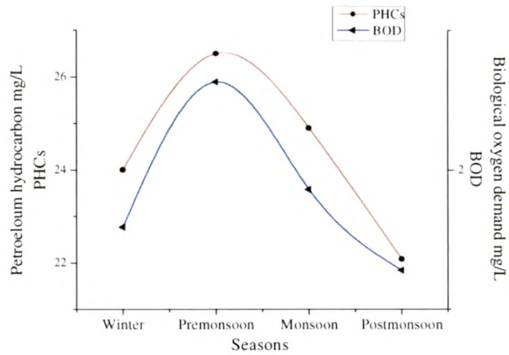
ALANG

Parameters	Phytoplankton Diversity	Zooplankton Diversity
PHCs	Yes*	Yes*
BOD	NS	NS

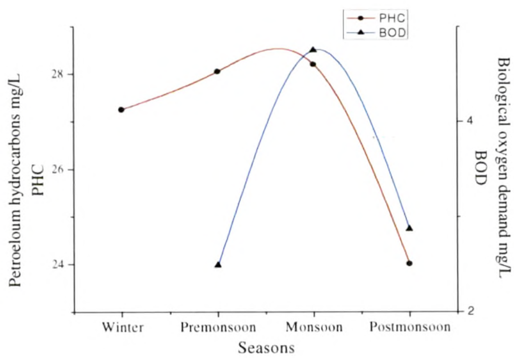
Yes* = The means are significant at $P \leq 0.05$ level.
NS= Not significant

Figure 5.1: Layout of the comparison of the petroleum hydrocarbon concentration and BOD during the four seasons at Diu, Veraval and Alang

5.1.1 DIU



5.1.2 VERAVAL



5.1.3 ALANG

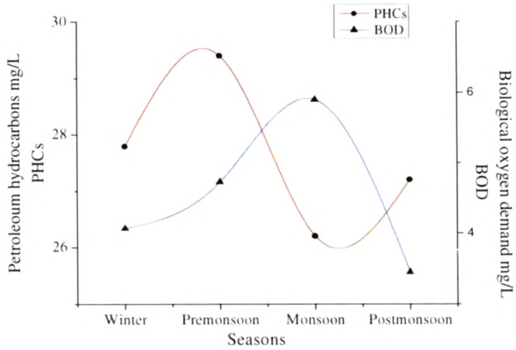
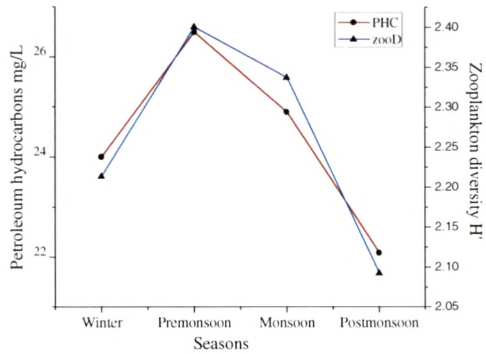
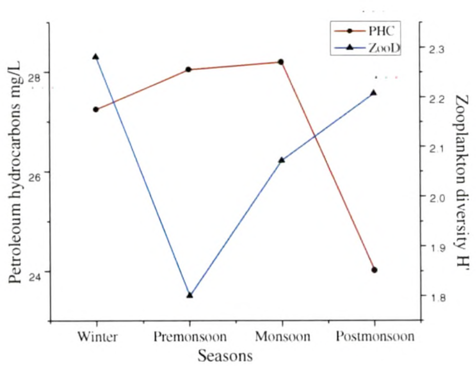


Figure 5.2: Response of zooplankton diversity to varying concentration of petroleum hydrocarbons during different seasons at Diu, Veraval and Alang

5.2.1 DIU



5.2.2 VERAVAL



5.2.3 ALANG

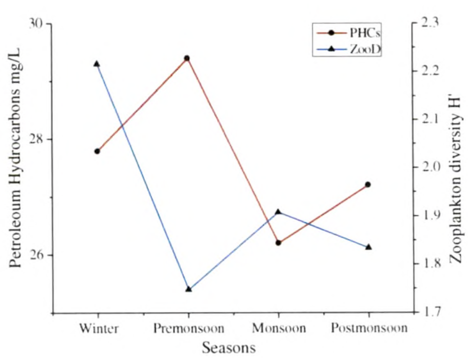
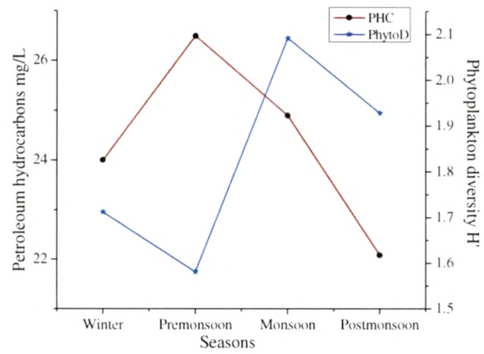
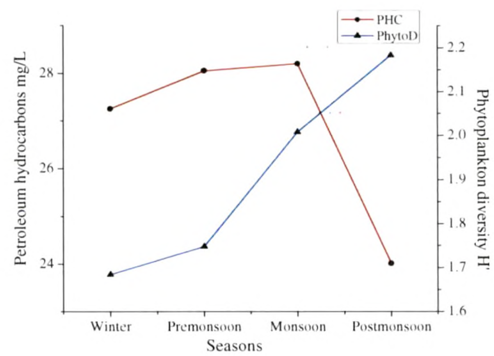


Figure 5.3: Response of phytoplankton diversity to varying concentration of petroleum hydrocarbons during different seasons at Diu, Veraval and Alang

5.3.1 DIU



5.3.2 VERAVAL



5.3.3 ALANG