Journal of Environment and Earth Science
ISSN 2224-3216 (Paper) ISSN 2225-0948 (Online)
Vol.3, No.14, 2013

Uncertainties assessment in marine ecosystem due to lowering of *p*H in coastal water of Bay of Bengal at Visakhapatnam, A. P., India

Vineeta Ghosh[1] and I. Nageswararao[1,2]
[1]Asian Marine Conservation Association (AMCA), 42/1, Feeder Road, Belgharia, Kolkata 700056, W.B., India
[2] Scientist-Member of AMCA; U.G.C. Research Scientist & Professor, Marine Chemistry Division, School of Chemistry, Andhra University, Visakhapatnam-530003, Andhra Pradesh, India, E-mail : inrao25@yahoo.co.in
*E-mail of the corresponding author : vineetaworldwide@yahoo.co.in

Abstract
Ocean acidification means the lowering of *p*H values below 7.0 presumably caused by the atmospheric CO_2 absorbance by seawater. Since coastal seawater allows to grow the respective ecosystem, which in turn allows them to absorb the atmospheric CO_2 releasing O_2 into the atmosphere, the excess CO_2 absorbance by seawater may lead to the change in the seawater chemistry by altering natural seawater *p*H, alkaline in nature, into lowering the same toward acidic-- keeping the possibility of alteration of marine and coastal ecosystem pathways leading to uncertainties in such ecosystem's productivity. The result of the experiment shows that the pH of the samples taken from different places of Visakhapatnam having two different ambiences (places/sampling spots from the open sea of Bay of Bengal and places/sampling spots from & nearby the Viskahapatnam natural port area) shows variations from each other. Open coastal seawater sample shows higher pH values as compared to that of harbour seawater. The rate of pH values determined in the subsequent year shows significant decrease in harbour seawater and having found a direct relationship with the dissolved oxygen content of the same. The result also shows that a very slight reduction of pH of the harbour seawater sample influenced in reducing the salinity, dissolved oxygen and total chlorophyll content.
Keywords: Marine & Coastal Ecosystem, Bay of Bengal, pH, Ocean Acidification, Salinity, Dissolved Oxygen, Total Chlorophyll.

1. Introduction

Our Earth is comprising of 5 systems : Hydrosphere, Atmosphere, Cryosphere, Geosphere and Biosphere. All these systems together have made this planet suitable habitat for living things to grow and develop as a result of continuous interactions amongst each other and thus made an overall planetary ecosystem suitable for all living things – from plankton to human being. Ocean, belonging to the hydrosphere, plays a crucial role by giving the shelter of enormous marine plants and phytoplanktons that produces O_2 by absorbing the CO_2 . This system of O_2-CO_2 cycle has been continuing from the time immemorial and there was no uncertainties. But with the progress of industrial revolution, human society has started to consume more and more energy which has lead to release of more CO_2 in the atmosphere. The ocean of the hydrosphere thus consume more CO_2 keeping the possibility of alteration of *p*H of the sea water (Caldeira & Wickett, 2003; Doney, 2006) by reducing the values of alkalinity toward possible acidity keeping the known coastal ecosystem function left into uncertain future (Khatiwala *et al*., 2009) and thus our general understanding of seawater chemistry involving various sets of carbonate reactions initiated with the dissolution of atmospheric CO_2 gas dissolve into seawater (Figure 1).

This paper based on the result of the present experiment shows that the pH of the samples taken from different places of Visakhapatnam having two different ambiences (places/sampling spots from the open sea of Bay of Bengal and places/sampling spots from & nearby the Viskahapatnam natural port area) shows variations from each other. Present experiment has been designed considering sampling spots of two different ambiences – one amongst those, however, the Visakhapatnam shipping port/harbour where energy consumptions appears to be too high and moreover, the oil spill of the surface seawater frequently occurs (Times of India Report, 2013; and many other references).

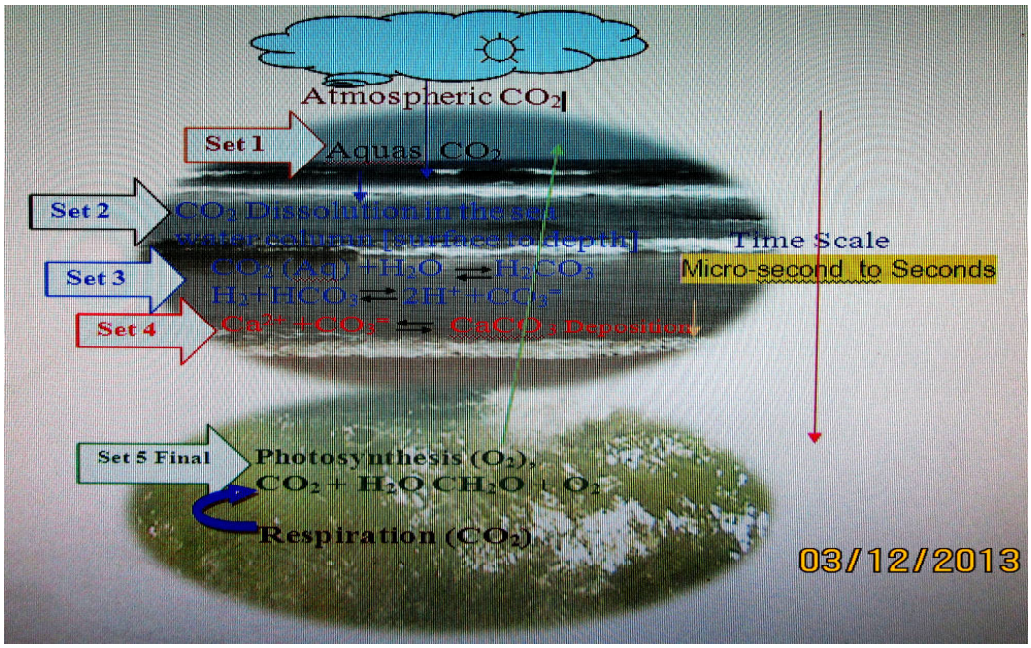

Figure 1. A series of CO_2 and carbonate reactions in air, seawater and sediment

2. Methodology

To provide the supporting scientific evidence of changing *p*H values in reducing trend of the seawater samples of various locations of Visakhapatnam, and assessing/predicting its possible impacts in a comparative basis, some other physico-chemical and biological determinations and observations were also carried out, however, in order to have idea on the effect of changing pH in the coastal ecosystem in the area under scientific investigation. As such, pH, temperature, relative humidity (RH), salinity, total chlorophyll and dissolved oxygen in the seawater samples from 7 open water locations and 3 Harbour locations were measured during winter periods (December – February of the year 2009-2010 and also the same period of 2010-2011 from the same locations.

2.1 Determination of Atmospheric relative Humidity

Atmospheric relative humidity direct reading was recorded from the digital RH meter [Model Digi-Ph-Ase]

2.2 Determination of Temperature

Measured in two ways : (a) by directly dipping the probe of two digital thermometers [manufactured by Eurolab and Multi-Thermometer] and (b) by precision mercury thermometer at the accuracy of $\pm$ 0.1˚C

2.3 Determination of pH

At the field pH was measured by digital pH meter [pHep, Italy] and at the laboratory by laboratory pH meter (Type Cl 46) fitted with the glass electrode , both calibrated with buffer 4.0 and 9.2

2.4 Determination of Salinity

The Mohr-Knudsen titrimetric method is adopted for the determination of chlorinity values, which were converted to salinity values by the UNESCO equation,

$$S^{\circ}/_{\circ\circ} = 1.80645 \text{ X } Cl^{\circ}/_{\circ\circ}$$

Principle involves comparison of precipitable halides (Cl^- and Br^-) in the sample to those precipitated by silver ions from a standard seawater . Seawater titrated with a solution of silver nitrate using potassium chromate as an indicator.

2.5 Determination of Dissolved Oxygen (DO, mg/L)

Dissolved oxygen (DO) in the seawater sample was determined by the modified Winkler's method. The principle involved is that dissolved oxygen in a measured volume of water is chemically bound by manganese (II) in a strong alkaline medium when the latter undergoes oxidation to manganese (IV). The DO was fixed in field. In presence of excess iodide, acidification leads to the liberalization of an equivalent amount of triodide, which can be titrated with the standard thiosulphate solution using starch as indicator.

2.6 Determination of Chlorophyll content

Pigments of phytoplankton were determined from the sea water by deploying the acetone extract of the pigments by spectrophotometric method as described by the Parsons *et. al* (1984). Cells of the phytoplankton were collected by filtering seawater on GF/C filters. Then filters transfer to 25 ml Stoppard glass bottles and extracted with 10 ml of Acetone (90%, GR quality) and then kept in refrigerator for 24 hours. The absorbance of clear Acetone extracts was measured by spectrophotometer by using 1 cm cuvette against reagent blank at different wavelengths (750, 664, 647, 630, 510 480 nm). Concentrations of chlorophyll '*a*', '*b*' and '*c*' and also carotene were then calculated using the equations as described by Parsons *et. al* (1984).

(C_a) Chlorophyll *a*= 11.85 E_{664} - 154 E_{647} - 0.08 E_{630}

(C_b) Chlorophyll *b* = 21.03 E_{647} - 5.43 E_{664} - 2.66 E_{630}

(C_c) Chlorophyll *c* = 24.52 E_{630} - 1.67 E_{664} - 7.60 E_{647}

2.7 Statistical Analysis :

Standard statistical analyses were carried out for computing all data in order to determine the mean values, standard deviations and standard errors. The analytical precisions calculated were at $\pm$ 0.5 to $\pm$0.7 for water temperature, $\pm$ 0.01 for pH, $\pm$ 0.5 to $\pm$ 0.7 for salinity $\pm$ 0.2 to $\pm$ 0.5, and for total chlorophyll $\pm$ 0.5 to $\pm$ 1.0. The result represented in figures shows only the mean values just to have the trend of pH values of the seawater under investigation.

3. Result & Discussion

It is evident from the Figure 2 and Figure 3 given below that the temperature of the surface sea water was found to be increased in the year 2010-2011 as compared to that of in the year 2009-2010 in both open coastal water and harbor water. But when compared the magnitude of temperature prevailed in open coastal water with that of the water of the port/harbour, the temperature determined in the open coastal water was found to be more pronounced as compared to that of the Port/harbour water which likely to occur as a reflection of heat absorbed in the respective coastal water. Sahuram *et al,* (1995) also found similar trend and relation of heat content and its reflection in temperature rise and explained the same a relationship which is directly proportional. They also worked considering the duration of the month of October-January/February. The magnitude of the mean temperature of the coastal seawater, in the present investigation, was found to be much lesser in magnitude as compared to that found by Sahuram *et al.,* (1995) which indicates that in addition to the temperature of the overlying air of the coastal seawater, other physico-chemical and/or biological factors are likely to involve and act as the driver in the temperature variations in coastal water of varying ambience considered.

It is interesting to note that while there was an increase in temperature and salinity from the year 2009-2010 to 2010-2011 which shows a positive relation but during the same period of observation and having the same ambience, the pH values were found to be lesser in magnitude by 0.01 unit in open coastal water from the period of 2009-2010 to 2010-2011 and by 0.02 unit in coastal water of harbour/port area. It is evident therefore that the decrease of pH values found from one year to the following year. It further appears from the result of the present experiment that the relationship between pH and temperature was found to be inversely proportional to each other. It is also evident that like pH-temperature relationship, the temperature-salinity relationship also was found to be inversely proportional to each other. In determining the dissolved oxygen (DO), it appears that the content of the DO in the open coastal seawater was found to be much greater in magnitude as compared to that of the same in the harbour/port area -- which is very likely as to the fact that the water of the harbour/port area is always having much biochemical oxygen demand (BOD) because of high organic load. Vertical mixing and long-shore current might be another source(s) of DO content in the open coastal water as compared to that of water from harbour/port area. In addition to those physical oceanographic parameter, the DO content of the open coastal water was also found to be increased as compared to that of the water of the harbour/port area. It is because of the content of the total chlorophyll was found to be at much higher magnitude in open coastal water as compared to that of the water of the harbour/port area. At least two factors might have played for this result. (1) In open coastal water, the maximum penetration of sunlight expectedly helped in more production of chlorophyll *'a'* (and thus the total chlorophyll content) that produced more quantity of oxygen as a function of photosynthesis which in turn have led to more DO content but (2) in the seawater of the port/harbour area the same was not possible because of (a) prevailing more turbidity due to wave breaking and (b) frequent release of petroleum oil fractions through spillage due to frequent sea-surface transport and other port activities (Kadam and Chauskey, 2002; Times of India, 2013), might have caused inhibition of photosynthesis by phytoplankton (Gordon and Prouse, 1973) or other metabolic inhibition in phytoplankton ultimately leading to death (Seyfettin

and Okus, 2007; Parab *et. al*., 2008) in the water of the port/harbour area. Death of such plankton community and also, the consumer community (that depends to live on these primary producers) finally come into the contact of the sedimentary system of overlying coastal water and produce organic matter causing to lowering the pH values in the surface water of the harbour/port area.

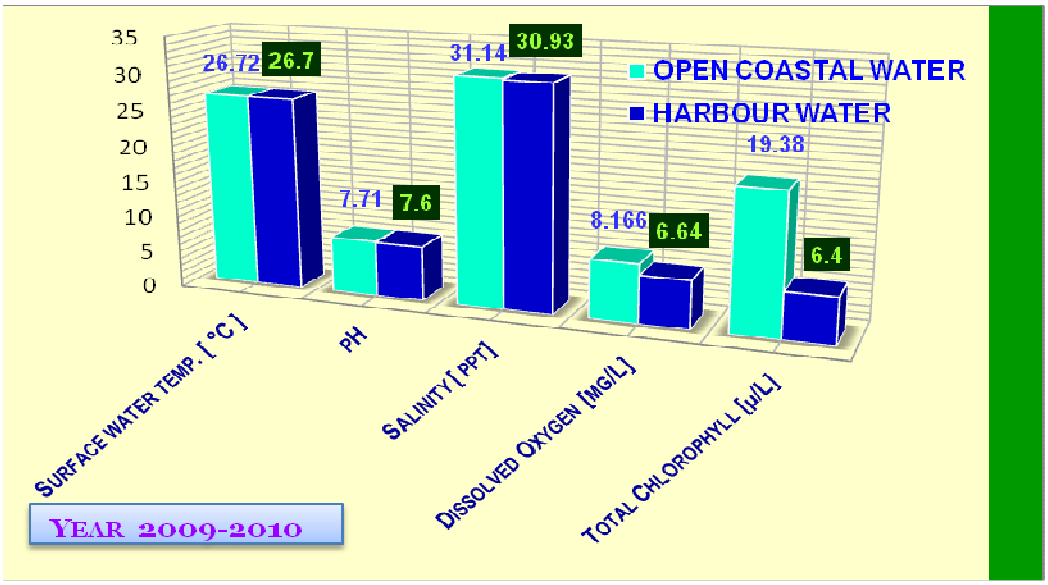

Figure 2. Comparative Assessment of properties of Coastal – Harbour water in 2009-2010

It is also evident that a direct relationship exists between the salinity, DO content and also total chlorophyll content. Although the total DO content (or, any part thereof) of the coastal water can otherwise be explained as a function of air-sea interfacial exchange of oxygen, in any experiment like the present one, it can not be denied that there exists a direct relationship between the total chlorophyll and the DO contents. Now, if it is considered that the oxygen production by the chlorophyll as a function of photosynthesis is true in a coastal water, it becomes a fact that the total chlorophyll content is directly proportional to the DO content. Therefore, combining all these factual circumstances while it is clear that salinity, total chlorophyll and DO content of any coastal water is important and any kind of perturbation in this function of ecosystem may alter the normal productivity of the respective coastal ecosystem.

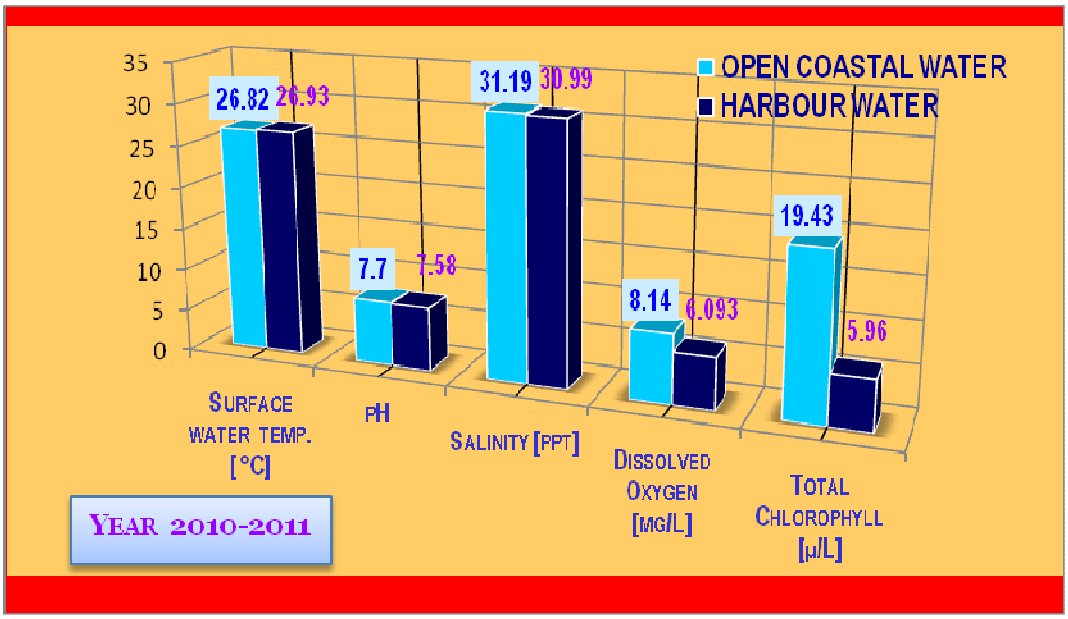

Figure – 3 Comparative Assessment of properties of Coastal – Harbour water in 2010-2011

In the open sea surface water sample, the lowering of pH value was found to be less pronounced as compared to the same of harbour water sample because of the very nature of the morphology of the Visakhapatnam harbor which is a semi-enclosed water bodies and such geo-morphological feature might have prevented the free mixing of open water from the offshore and have therefore caused the lowering of *p*H of the sea water in more profound manner (Figures 2) which might have happened by increase in petroleum oil fraction in the harbour water causes the death of phytoplankton or producers which in turn caused the depletion of DO content in the respective water which could not have been compensated from free mixing of fresh seawater from open deep sea because of the morphological feature of the Visakhapatnam harbour area. The degree of such lowering values of pH was found to be increased a year later also (Figures 2 & 3). On the whole, the mechanism appears to be posing a negative impact on the overall mechanism of the coastal ecosystem functioning due to lowering of *p*H and can diagrammatically described in the following :

Decrease in *p*H leads to ➡ decrease in chlorophyll content, that in turn causes to ➡ decrease in dissolved oxygen content

It is evident (Figures 2 and 3) that dissolved oxygen (DO) content was found to be in reducing trend from the period of 2009-10 to 2010-11. Even amongst the magnitude of such reduction, DO content in harbor water was found to be more pronounced as compared to that of the open coastal water (Figures 2 and 3). Given the fact that the prolonged oxygen depletion in the coastal water may cause widen mortalities of marine/coastal organisms (Diaz and Rosenberg 1995), the prevailing situation found in Visakhapatnam area appears to be of much concern for the primary production and other subsequent coastal ecosystem functioning upon which many socio-economic growth (like fish & fishery production, tourism activities etc.) and development of this area depend.

It is the very fact that the harbor water retains a severe petroleum oil fraction (The Hindu, 2012; Times of India, 2013) and that might have caused the death and partial extinction of coastal aquatic plants and planktons and other living creatures (Mohan and Prakash, 1998) causing the increase in organic carbon content including organic acid in the marine water and sediment of this area. This in turn (through sediment-water interface come to influence the overlying surface water and finally), might have reduced the *p*H of the water sample taken from this area which might have been possible due to the fact that marine fulvic acids are a major pool of organic carbon (McKnight *et al*., 1991).

If such situation continues, or allowed to be continued – the magnitude of lowering of the pH of the coastal water of the Visakhapatnam harbour area would be increased. If pH would be continued to be lowered, even in a greater time-scale, the primary productivity and normal sustainability in the coastal ecosystem would be disrupted, and so would be the other characteristics of coastal seawater such as salinity of the water and sediment. Thus, the coastal ecosystem of this part would be facing uncertainty(s) at least in : (a) primary production, (b) production of oxygen and content of dissolved oxygen in coastal seawater, and thus (c) increasing BOD, (d) gradually alteration of normal coastal ecosystem including the fish and fishery production in this part, and so on……..that are yet to experience.

4. Conclusion and Recommendation

Although the detail analysis of the socio-scientific & economic results is out of the scope for this paper, even then having found a trend of the study of the present investigation, it can be concluded that a detailed decade-long socio-scientific investigation is very much required for assessing the impact of this area emphasizing the study on the release of CO_2. This is necessary to determine of the exact nature of uncertainty(s) of the reducing pH of the seawater here from alkaline range toward acidic -- because of the fact that the risk of irreversible ecosystem changes due to ocean acidification should enlighten the ongoing CO_2 emissions debate (Guinottea and Fabry, 2008) and also ocean acidification's economic consequences for commercial fisheries (Cooley and Doney, 2009).

It is revealed from the present investigation that the trend of lowering value of *p*H not only occurred in the harbor water, but also in the open seawater. Since there are reports on the highest traffic volume of about 38.22

million tones in the seaport (VUDA, 2007), it is likely that the energy consumption releasing CO_2 into the ambient atmosphere are to be increasing in trend at present, and so is increasing the probability of the magnitude of CO_2 dissolution into surface seawater. Such situation, if continues, may have a definite role in reducing the *p*H of the surface seawater. Taking both the situations (of harbor water and open coastal water) into account, it appears that the *p*H of the sea water of Bay of Bengal in this area, on the whole, is presently having tendency to be lowering in trend which would have enough potential to alter the normal coastal ecosystem functioning -- if not taken immediate care of by preventive measures.

References

Caldeira, K. and Wickett, M. E. (2003). Oceanography: Anthropogenic carbon and Ocean pH. *Nature* Vol. 425, 365-365 (25 September 2003)

Cooley, S. R. and Doney, S. C. (2009). Anticipating ocean acidification's economic consequences for commercial fisheries. Environmental Research Letters, 4(2) : Art. 024007.

Doney, S. C. (2006). The Dangers of Ocean Acidification. Scientific American, Page 58-65.

Diaz, R.J. and Rosenberg, R. (1995). Marine benthic fauna: A review of its ecological effects and the behavioral responses of benthic macrofauna. *Oceanography and Marine Biology Annual Review* 33: 245-303.

Gordon, D. C. Jr., and Prouse, N. J. (1973). The effect of three crude oils on marine phytoplankton photosynthesis, *Marine Biology* 22, 329-333.

Guinottea and Fabry, (2008). Ocean Acidification and Its Potential Effects on Marine ecosystems, *Ann. N.Y. Acad. Sci*. 1134: 320–342.

Kadam, A. N. and Chauskey, M. K., (2002). Status of oil pollution along the Indian coast, Proc. The National Seminar on Creeks, Estuaries and Mangrove – Pollution and Conservation, Nov. 2002, 12-16

Khatiwala, S, F. Primeau & T. Hall (2009). Reconstruction of the history of anthropogenic CO_2 concentrations in the ocean, *Nature* 462, 346-349 (19 November 2009) |

McKnight Diane M., Aiken George R. and Smith, Richard L., (1991). Aquatic fulvic acids in microbially based ecosystems: Results from two desert lakes in Antarctica*, Limnol. Oceanogr*, 36(5), 1991, 998-1006, © 1991, by the American Society of Limnology and Oceanography, Inc.

Mohan, P.C. and Prakash, R. R. (1998). Concentration of Petroleum Hydrocarbons in Bivalve *Mytilopsis sallei* and in the Harbour Waters of Viskahapatnam, East Coast of India, Indian Journal of Marine Sciences, 27, 496-498.

Parab, Sushama R., Pandit, Reena A., Kadam, Arun N. and Indap, Madhabi M. (2008). Effect of Bombay high crude oil and its waer soluble fraction on growth and metabolism of diatom *Thalassiosira* sp. Indian Journal of Marine Sciences, Vol 37(3) September 2008, pp 251-255.

Parsons, T. R., Y. Maita and Lalli, C. M., (1984). A manual of chemical and biological methods for sweater analysis. Pergamon Press.

Sahuram, Y., Prabhakara Rao, B., Rao, D. P., and Subba Rao, V. (1995). Spatial and temporal variability of the heat budget parameters and currents in the coastal waters of Viskahapatnam, east coast of India, *Indian Journal of Marine Sciences,* Vol. 24, June 1995, pp. 82-86.

Seyfettin Tas and Erdoˇgan Okus (2007). Effect of oil pollution on the phytoplankton community in the Kucukcekmece Bay (North-Eastern Sea of Marmara, Turkey), *Rapp. Comm. int. Mer Medit.,* 38, pp 320.

The Hindu, (2012). *Study confirms high ocean pollution due to oil spillage*, online publication, Visakhapatnam, July 3, 2012

Times of India, (2013). *Industrial effluents choke marine life, 'Polluted Vizag'*, TOI Visakhapatnam Publication, 22nd January, 2013

VUDA, (2007). Revised Master Plan for Visakhapatnam Metropolitan Region – 2021, April, 2007.