

**Nabil, Al-Shwafi, Abdulhakim Mohsen Ahmed**

Sana'a University-Faculty of Science

Department of Applied Ecology Faculty of Ecology and Physics of natural environment

Russian State Hydrometeorology University

## **A SYSTEMATIC EVOLUTION OF SELECTED NUTRIENT AND CHLOROPHYLL – A ALONG OF HADRAMOUT COAST-YEMEN**

*The hydrographical parameters: air, water, Salinity, dissolved oxygen, pH and total alkalinity of the coastal waters in front of Hadramout, were determined. The results obtained reflect the effect of the warm tropical zone of the Gulf of Aden and the Arabian Sea, irregular topography, local hydrographic condition and the result of upwelling current.*

*Seawater samples were seasonally collected from the coastal surface water along of Hadramout coast of Yemen during October, 2000 and analyzed for determination of the concentration of nitrite, nitrate, reactive phosphate, silicate and chlorophyll-a. The concentrations in October corresponding to the up-welling in the Gulf of Aden and Arabian Sea and from land-based activities. Hadramout coast is also more productive in comparison to the open waters maximum values.*

### **Introduction**

The most predominant overwhelming feature of the Gulf of Aden coastal regions which affects every aspect of the present day physical, biological and socio-economic environs is the fact that the area is a desert.

The Yemen coast is characterized by a narrow coastal plain between the Gulf of Aden and the mountain range that parallels the shoreline. This range averages 1.070 m in height and influences the local weather, especially the wind (ba-Sumaid, 1997).

The Yemen coastal region is influenced by two distinct monsoon seasons. The months of April, May, September and October are transitional months as global pressure patterns re-adjust to the changing incoming solar energy (Noval Oceanography Command Detachment, 1982).

The climate of the Yemen coast and nearby waters is dominated by hot and extremely arid conditions characteristic of North Africa and peninsula (Howe, *et al.*, 1968). The area of the Gulf of Aden/ Arabian Sea needs intensive hydrographical study. Consequently, the present work was undertaken to study the hydrographical parameters: air and water temperature, Salinity, dissolved oxygen, hydrogen ion concentration and total alkalinity in the Gulf of Aden/ Arabian Sea water in front of Al-Mukalla. Therefore, the results of these investigations could be considered as pilot for further similar studies in the coastal waters of Gulf of Aden/ Arabian Sea.

The high primary productivity, due in part, to the upwelled nutrient, support a feed web which ultimately sustains the fish community. The seasonally of the monsoon winds drive the upwelling and, in turn, cause a seasonal periodicity throughout the food web.

Among the component of wastewater, most likely to have an impact on marine ecosystem, are nutrients, organic matter and microorganisms. Several literature reports described the occurrence of eutrophication as a result of high concentration of nutrients chemicals in the coastal waters (Cederwall & Elmgren, 1980; Rosenberg, 1985; Degobbi, 1989). Eutrophication is defined as an increase in nutrients, which usually lead to increased growth of algae and plants. There are good reasons to believe that eutrophication can in the near future become a common hazard in marine coastal areas in many parts of the world. Such a process would have damaging effects on both inshore fisheries and recreational facilities. Monitoring major nutrient levels, therefore, is important to assess the pollution degree and/ or the quality state of water resources (Hassan *et al.*, 1995; Friligos, 1985; Rosenberg, 1985; Zoffmann *et al.*, 1989). Riley *et al.*, (1978) reported that, the range of nutrient concentrations in marine water under normal environmental conditions are as follows ( $\mu\text{g/l}$ ): nitrate, 1.0-120; phosphate, 1.0-160; ammonia, 0.0-50 and nitrite, 0.2- 30.

### Material and Methods

#### ***The area of study, situated in the coastal surface seawater in front of Hadramout beach for about 200Km from west Broom to east Al-Shafer.***

Five sections perpendicular to the coast were selected to cover the study area (Fig.1). Sampling was carried out in 11-13 October 2000 (autumn).

Air, water temperature were measured at the time of sampling, using standard reversing protected thermometers, with accuracy of  $0.01\text{C}^\circ$ . Water samples were collected in dark bottles and kept in dark box for salinity, pH and alkalinity determination in the laboratory. Dissolved oxygen was analyzed according to the modified Winkler's method, Salinity of each sample was analyzed against Copenhagen Standard Seawater at the Department of Earth and Environmental Science, Sana'a University. The titration method described by Grassoff, (1982) was used. Total alkalinity of each sample was determined by the method of Anderson and Robinson, (1964) as developed by Culberson, (1970).

The combination electrode was standardized with pH. 4.00 and pH 7.00 buffers at  $25\text{C}^\circ$ . The pH of each sample was calculated from:

$$\text{pH}_{\text{sw}} = (E_{\text{sw}} - E_4) / S.$$

Where  $\text{pH}_{\text{sw}}$  is the pH of the ample,  $E_{\text{sw}}$  and  $E_4$  are the measured potential of the sample and 4.0 buffer, respectively, and S is the measured slope of the electrodes obtained from:

$$S = (E_4 - E_7) / (4.00 - 7.00).$$

Where  $E_7$  is the measured potential of the buffer solution 7.00. The slope of the electrode response was constant over long periods, and measurements of 7.00 buffer were made at the beginning and the end of the day. All measurements of pH and total alkalinity were made at  $25 \pm 0.1\text{C}^\circ$  where the samples were placed in water bath for 10-20 minutes before measurements. The pH-meter used was digital pH/mV meter. The precision of the measurements were  $\pm 0.01$  pH and  $\pm 0.009$  meq  $\text{l}^{-1}$  for alkalinity.

### **Sample Collection**

In order to give an even coverage of Hadramout coast, coastal water samples were collected from five stations. At each occasion near shore water was obtained from the surface by means of a polypropylene reversible water sample (Van Dorn). After collection the seawater was filtered through Whatman GF/C Millipore filter papers (0.47 $\mu$ m) and stored in acid washed polypropylene or glass polystop bottles.

Water samples were kept on ice in a field cool box till return to the laboratory where they placed in a deep freeze (about  $-20^{\circ}\text{C}$ ). Later on samples were transported to the analytical laboratory for the determination of nitrite, nitrate, phosphate, silicate and chlorophyll-a according to the Standard Chemical Methods for Marine Environmental Monitoring (UNEP, 1988) and Weilder, (1974).

All chemicals used in the present survey were high purity analytical grade. Double distilled water and/or deionized water used for preparing, standards and dilution of samples. Blank determinations were carried out for each group of sample on a monthly basis.

Spectrophotometer Model Spectronic 501 supplied by Milton Roy was used to measure absorbency at the recommended wavelength.

#### *Nitrite*

Nitrite determination in the sampled water was carried out according to that of Grasshoff (1983).

#### *Nitrate*

The method employed in the present study was based upon the reduction of nitrate to nitrite by allowing the water sample to pass through a column packed with copper-coated cadmium. The later was determined colormetrically via the formation of an azo dye (Grasshoff 1983).

#### *Reactive phosphate*

The determination of dissolved inorganic phosphate in seawater samples collected during the present survey was according to the method described by (Murphy and Riley 1962). This method is based on the formation of a highly colored blue phospho-molybdate complex. The modification brought by Koroleff (1983) was also taken into account.

#### *Reactive Silicate*

Determination of reactive silicate in the Red Sea waters was carried out according to the method described by Koroleff(1983).

#### *Chlorophyll-a*

The estimation of chlorophyll-a was carried out according to the method described by Weider(1974).

## Results and Discussion

### 1 – Air temperature:

It ranged between 27.5 and 28.0C° with a mean of 27.72C°. The minimum value is at station 1, while maximum value is at station 4. The difference between the air temperature is due to a strong decrease in mean surface temperature in the eastern Gulf of Aden during these months as a result of upwelling current off Somalia (Naval Oceanography Command Detachment, 1982).

### 2 – Water temperature:

It ranged between 28.1 and 29.0C° with a mean of 28.44C°. The minimum value is at station 3, while the maximum value is at station 4. Such distribution indicates that the inshore surface waters is affected by upwelling current off Somalia.

Both air and sea surface temperature peak in June but dip in July and August relative to the June and September temperature (ba-Sumaidi, 1997).

### 3 – Salinity (S‰ = ppt):

The salinity readings showed no more difference, the lowest value is at station 4, while the highest value at station 1. These variations may be mainly due to local hydrographic conditions for example semi-isolated, intensive evaporation and restricted circulation, (GEF, 1999; Al-Shwafi, 2001).

### 4 – Dissolved Oxygen (D.O):

The surface water of the Gulf of Aden and the Arabian sea along the coast of Yemen contained sufficient amount of dissolved oxygen (Table, 1). Dissolved oxygen values ranged between 3.6 mg/l at station 3 to 4.5 mg/l at station 5. These fluctuations may be attributed to several hydrographic and biological conditions prevailed at various locations.

### 5 – Hydrogen Ion concentration (pH):

The surface horizontal (geographical) distribution of pH is shown in Table1. The general pattern of the surface horizontal distribution of pH gave local variation mainly due to the climatic conditions, and consequently water temperature, as well as dissolved oxygen content and biological activity, (Hanna, *et al.*, 1988).

### 6 – Total alkalinity (T.A)

The total alkalinity values varies from 2.331 at Rayan to 2.390 at Al-Shaher and the mean value is 2.366 meq l<sup>-1</sup>. These values of total alkalinity are possibly caused by the mixing processes and temperature increase which both expel CO<sub>2</sub>; and photosynthesis processes. The photosynthesis processes is confirmed by the high values of O<sub>2</sub> content of surface seawater (Rushdi, personal communication).

The levels detected for nitrate, nitrite, phosphate, silicate ions and chlorophyll-a showed wide fluctuations, however most values were within the expected levels present in surface sea waters as described by Riley *et al.*, (1987). Some of the sampling sites are near fishing and commercial marine routs or anchorage zone boats, ships and

tankers.in addition due to upwelling activities observed in Gulf of Aden and Arabian Sea (Thangaraja, 1990). It is of interest to mention that red tide blooms have also been observed in these sites.

7 – Nitrite ( $\text{NO}_2^-$ -N)

It is intermediate state between oxidation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  in nitrification and the reduction of the  $\text{NO}_3^-$  to either  $\text{N}_2\text{O}$  /  $\text{N}_2$ -molecules or  $\text{NH}_4^+$  in denitrification or N-immobilization (Santschi *et al.*, 1991). Its mean concentration rang from 10.3  $\mu\text{g}$  at N-  $\text{NO}_2$ / kg in station 1 to 13.50 $\mu\text{g}$  at N-  $\text{NO}_2$ / kg in station 5.

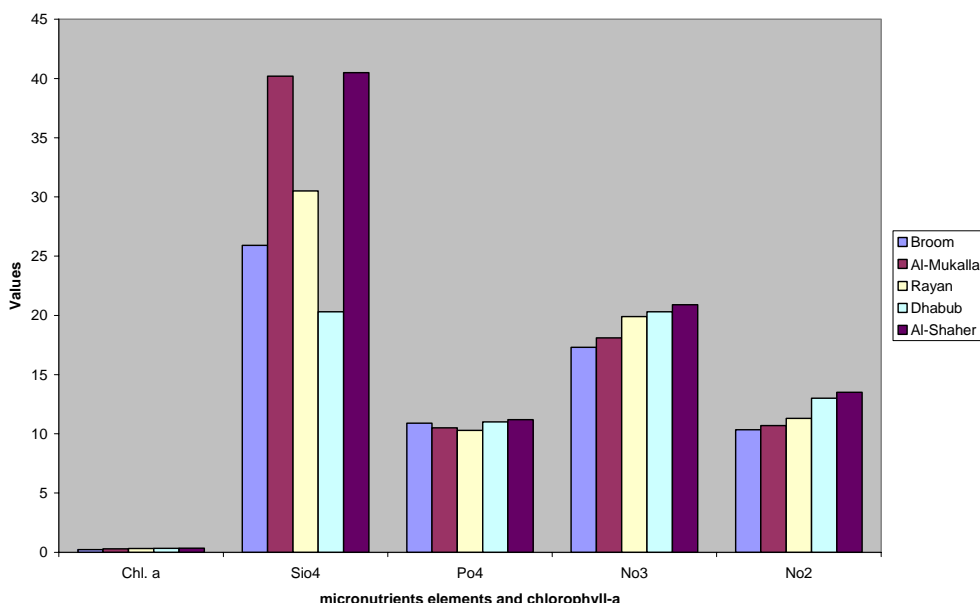
The last is detected in the surface waters of station1, that shoes low values of salinity, dissolved oxygen and transparency suggesting the input of nitrite is accompanying the sewage from the outfalls (Table, 2 and Figure, 3).

Table 2

**Mean concentration of micronutrient elements and chlorophyll in the study area**

No2	No3	Po4	Sio4	Chl. a	Location
10.34	17.3	10.9	25.9	0.23	Broom
10.7	18.1	10.5	40.2	0.293	Al-Mukalla
11.3	19.9	10.3	30.5	0.312	Rayan
13	20.3	11	20.3	0.33	Dhabub
13.5	20.9	11.2	40.5	0.34	Al-Shaher

**Fig.3: Mean concentration of micronutrient elements and chlorophyll-a in the sudy area**



8 – Nitrate ( $\text{NO}_3^-$ –N)

Nitrate is the final Oxidation State (nitrification) of other nitrogen compounds in the oxic seawater having high redox potential. Highest mean concentration  $20.90\mu\text{g}$  at N-  $\text{NO}_3^-/\text{kg}$  was encountered in station 5 to  $17.30\mu\text{g}$  at N-  $\text{NO}_3^-/\text{kg}$  was encountered in station 1.

9 – Reactive phosphate ( $\text{PO}_4^{3-}$ –P)

The phosphate concentrations in the different sites also not a wide varying range between  $10.30$ – $11.20\mu\text{g}$  at p- $\text{PO}_4^{3-}/\text{kg}$  in July, lower phosphate concentrations were detected in al-Rayan and high phosphate concentrations were detected in Al- Shaher. Phosphate levels were markedly high during the sponge season particularly in sites, which have shallow water.

It's ranges in marine water under normal conditions are  $1.0$  to  $160\mu\text{g}/\text{kg}$  (Riley *et al.*, 1978). It is probably at this time of the year that most of the microbial degradation and release of such compound in the water might take place particularly in shallow waters where bottom sediments are usually thriving with microbial counts detected in water samples from these sites.

10 – Silicate ( $\text{Si SiO}_2$ )

The distribution of reactive silicate along Hadramout coast is shown in (Table, 2 and Figure, 3). Silicate fluctuation in surface water coincide to certain extend with that encountered in surface water. The highest silicate mean concentrations determined during the present survey had varying range between  $20.30$ – $40.50\mu\text{g}$  at  $\text{Si SiO}_2/\text{kg}$ , lower silicate concentrations were detected in Al-Dhabah and high silicate concentrations were detected in Al- Share. This reflects the fact that the major source of silicate is up- welling and sandstorms.

11 – Chlorophyll-a

The amount of chlorophyll-a estimated in Hadramout coast is presented in (Table, 2). The highest concentrations were encountered in station 5,  $0.340\text{ mg}/\text{l}$  and lower concentrations were encountered in station 1,  $0.230\text{ mg}/\text{l}$  and  $0.140\text{ mg m}^{-3}$  for surface water. However, (No clear pattern could be established) for chlorophyll-a fluctuations. These may be mainly due to the abundance of phytoplankton, sea grass and others primary producers.

The pelagic productivity is low, because of the formation of thermocline and halocline that prevents the recycling of nutrient from deeper water to the euphotic zone, and there is little nutrient input to the pelagic system from land surface run-off (Weikert 1987). Primary production increases from north to south (Halim 1984) following the pattern of nutrient distribution mentioned earlier in addition to the fact that beside nutrient, plankton (phyto and zooplankton) are also transported by water masses from the Gulf of Aden to the southern Red Sea (Halim 1969). Studies on primary productivity in the central Red Sea indicated that productivity is close to  $170\text{-mg C m}^{-2} \text{ d}^{-1}$  (Dowider 1983; Weikert 1987). According to Koblenz- Mishke *et al.*

(1970), north of about 17<sup>0</sup> N, The average annual production in the euphtic zone ranges within 250 to 500 mg C m<sup>-2</sup>d<sup>-1</sup>, but in the southern most part of the basin, within 500 to more than 1,000 mg Cm<sup>-2</sup>d<sup>-1</sup> were reported (Weikert 1987). This would classify very productive waters.

Table 1

**Mean of air and water temperature, salinity, pH and total alkalinity in the Hadarmout coast**

No.	Location	Air temp.	Water temp.	Salinity	Dissolved O <sub>2</sub>	PH	Total Alkalinity
1	Broom	27.50	28.30	36.40	4.00	8.00	2.378
2	Mukalla	27.70	28.50	36.22	3.90	7.88	2.360
3	Rayan	27.90	28.10	36.11	3.60	7.83	2.331
4	Dhabuh	28.00	29.00	36.09	4.30	7.95	2.373
5	Al-Shaher	27.50	28.30	36.10	4.50	8.01	2.390
	Mean	27.72	28.44	36.148	4.06	7.93	2.336
	Range	27.50-28.0	28.10-29.00	36.09-36.40	3.60-4.50	7.83-8.01	2.331-2.390

Table 2

**Mean concentration of micronutrient elements and chlorophyll-a in the Hadramout coast**

No.	Location	No <sub>2</sub>	No <sub>3</sub>	Po <sub>4</sub>	SiO <sub>4</sub>	Chl. a
1	Broom	10.34	17.30	10.90	25.90	0.230
2	Al-Mukalla	10.70	18.10	10.50	40.20	0.293
3	Rayan	11.30	19.90	10.30	30.50	0.312
4	Dhabub	13.00	20.30	11.00	20.30	0.330
5	Al-Shaher	13.50	20.90	11.20	40.50	0.340
Mean		11.77	19.30	10.78	31.48	0.301
Range		10.34-13.50	17.30-20.90	10.30-11.20	20.30-40.50	0.230-0.340

**References**

- Al-Shwafi, N.* (2001). Beach tar along the Red Sea coast of Yemen “Quantitative Estimation and Qualitative Determination”, ph.D Thesis, Dep. Earth and Environmental Science, Fac. Sci., Sana’a Univ, 186 p.
- Anderson, D.H. and Robinson, R.J.* (1964). Rapid electrometric determination of the alkalinity of sea water using a glass electrode. *Ind. Eng. Chem. Analyst. Edit.* 18: 767-769.
- Ba-Sumaid, A.A.* (1997). Effects of Masila oil Terminal on coastal Fauna M.Sc. Thesis, Dep. Biology, Fac. Sci, Sana’a univ, 133 p.
- Cederwall, H. and R. Elmgren* (1980). Biomass incase of Benthic macrofauna Demonstrates Eutrophication of the Baltic Sea. *Ophelia Supplement* 1: 287-304.
- Culbertson, C.* (1970): Seawater alkalinity determination by the pH method. *J Mar. Res.* 28(1): 15-21.
- Degobbi, D.* (1989). Increase Eutrophication of the Northern Adriatic. *Sea: Secona Act. Marine Pollution Bulletin* 20: 452-457
- Dwoider, N. M.* (1983). Primary Production in the central Red Sea off Jeddah, In: (Latif, A. F., Bajoumi, A. R., and Thompson, M. F., eds.). *Proceedings of the International Conference on Marine Science in the Red Sea. Bulletin of Institute of Oceanography and Fisheries* 9: 160-170.
- E.S. Hassan, I.M. Banat, S. El-Shahawi and A.H. Abu-Hilal* (1995). Asystematic Evolution of Selected Nutrients, Heavy Metals and Microbial pollution Along the east Coast of the UAE.J. *Fac. Sci., U.A.E Univ.*, 17:203-226.
- Frigilos, N.* (1985). Nutrient Conditions in the Euboikos Gulf (West Aegean). *Marine Pollution Bulletin* 16: 435-439.
- Grassoff, K.* (1982): *Methods of seawater analysis.* 2nd Edition. Verlag Chemie, 419 p.
- Global Environmental Facility (GEF)* (1999). *Distribution of Micro-nutrient Element in the Red Sea coast of Yemen.* 28 p.

- Grasshof, K.* (1983). Determination of Nitrite. In: Grasshoff, K., Ehrhardt. M., Kremling (eds), *Methods of Seawater Analysis*, Verlag Chemic, Weinheim, 143-150.
- Halim, Y.* (1969). Plankton of the Red Sea. *Oceanogr. Mar. Biol. Ann. Rev.* Vol. 7 : 231-275.
- Halim, Y.* (1984). Plankton of the Red Sea and the Arabian Gulf. *Deep Sea.* Vol.31: 969-982.
- Hanna, R.G.M.; Saad, M.A.H. and Kandeel, M.M.* (1988). Hydrographical studies on the Red Sea water in front of Hurgada, *Marina Mesopotanica* 2: 139-156.
- Howe, G.H.; Reed, L.J.; Ball, J.J.; Fisher, G.E. and Lasso, W.G.B.* (1968). Classification of world desert areas. Report 69-38ES, Earth Science laboratory, United States Army Natick, laborites Natick, MA.
- International Conference on Marine Science in the Red Sea. *Bulletin of Institute of Oceanography and Fisheries* 9: 160-170.
- Koblentz-Mishke, O.J., Volkovinsky, V.V. and Kabanova, J.G.* (1970). Plankton Primary Production of the world ocean. In *Scientific Exploration of the South Pacific*. Ed. W. s. Wooster, pp. 183-193. National Academy of Science, Washington.
- Koroleff, A.S.* (1983). Detremination of phosphate. In: Grasshoff, K., Ehrhardt. M., Kremling (eds), *Methods of Seawater Analysis*, Verlag Chemic, Weinheim, 151-155.
- Murphy, J. and riley, J. P.* (1962). A modified single solution method for the determination of phosphate in natural waters. *Analytical Chimica Acta.* V. 27: 31-36.
- Naval Oceanography Command Detachment (1982): Climate study of the near coastal zone, Red Sea south and Gulf of Aden. U.S. Naval Oceanographic command Detachment, Asheville, NC.
- Riley, J.P.* (1978). Nutrient Chemicals (including those derived detergents and agriculturaichemicals). In: *A Guide to Marine Pollution*. (Goldberg, E.D., ed). Gordon and Beach Science Publishers, New-York, London, Paris.
- Rosenberg, R.* (1985). Eutrophication the future Marine Coastal Nuisance. *Marine pollution Bulletin* 16: 227-231.
- Santschi, P.H.; Benoit, G. and Brink, M.B.* (1990). Chemical processes at sediment-water interface. *Mar. Chem.*, 30: 269-315.
- Thangaraja, M.* (1990). Studies on Red Tides of Oman. Marine Science and Fisheries Center (MSFC) Research Report No.90-2. Ministry of Agriculture and Fisheries, Muscat, Sultanate of Oman. 18 pp.
- UNEP, U.S. Environmental Protection agency, (1988). *Methods for Chemical Analysis of water and Wastes*, UNEP Technology Transfer EPA-625-16-74-003a, Washington.
- Weikert, H.* (1987). Plankton and the pelgic Environment. In.: (Edwards, A. J. and Head, S.M. (Eds.) *Key Environment. The Red Sea*. Pergamon Press, Oxford. 90-111.
- Weilder, R.A.* (ed) (1974). *A Manual on Methods for Measuring Primary Production in Aquatic Environments*, IBP Handbook No. 12. Blackwell Scientific.
- Zoffmann, C.F. Rodriguez-Valera, M. Perez\_fillol, F. Ruia-Bevia, M.* (1989). Torrebance and F. Colom, *Microbial and Nutrient Pollution Along the Coasts of Alicante, Spain* *marine Pollution Bulletin.* 20: 74-81.