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Studies On Nutrients And Hydrography Parametres In Visakhapatnam Harbor Waters.

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Abstract: *The Visakhapatnam harbor is a natural harbor and also is a leading major port in India. Due to urbanization and fast industrialization more amounts of domestic sewage and industrial effluents are entering in to harbor waters. The harbor attains strategic importance in recent years because of its utility is not only commerce but also in defense. In Visakhapatnam large number of industries such as oil refinery, fertilizer units are located in the vicinity of the harbor. Thus the author attempts to analyze the hydrological parameters of temperature, pH, salinity,Dissolved oxygen and nutrient parameters of ammonia,nitrite, nitrate and chlorophyll 'a'. the impact of nutrient pollution and assessment of eutrophication on the quality of Visakhapatnam harbor has been studied.*

Keywords: *Anthropogenic, Eutrophication, Harbor Water, Nutrients, Phytoplanktons*

I. Introduction

India is a country developing fast industrially and agriculturally. A consequence of the former is urbanization and of the latter, denudation of the forest cover. Both have a telling effect on the quality of the environment. The sea, which represents a regime of the lowest potential energy, receives all types of influxes carrying industrial, agricultural and urban wastes; hence its water quality is affected and thereby its living organisms. Unlike in the case of seas, e.g., the Mediterranean bordering highly industrialized countries, Indian seas are not as much polluted by these effluents, except at certain point locations (a recent review on present status of marine pollution (Qasim &Sen Gupta,1980;). This is a good starting point for evolving (and implementing) methods of pollution abatement followed by a long-term protection policy of the coastal waters. Usually, many industries are located on river banks, back waters and harbors etc. , for an easy disposal of their wastes. The harbors in addition to being used as ports are often used as points of discharge of effluents from industries, sewage and agriculture, etc.In recent years there has been a rapidly growing interest on the study of heavy metal content in coastal and harbor, its behavior and the pathways by which they are introduced into the system. Well known that harbors and estuaries of the world are the region heaviest pollution by heavy metals (Forstner and Wittmann, 1981). The physico-chemical processes which act soil of the catchment area normally control the concentration of trace metals in the fluvial and sediments. Due to anthropogenic input, abnormal concentration of heavy metals in both dissolved and particulate phases of the harbor waters. These high inputs can also affect the adjoining coastal waters due to exchange. Addition of these undesirable heavy metals in excess quantities can disrupt the delicate balance which exist between biomass and trace metals. When it exceeds tolerance level, certain species in aquatic organisms will perish. Certain aquatic organisms have the ability to concentrate toxic metals many fold in their body which ultimately passes on to human beings through marine food web causing deleterious effects to human beings.

II. Materials And Methods

Visakhapatnam harbor is divided into 5 stations they are,
Station 1, is located in the centre of the **outer harbor.** The average depth of this station is about 18 meters. A finger type Jetty is situated in this region for loading iron ore into export vessels of as high as 1 lakh DWT.
Station 2, is located in the centre of the **entrance channel**. This is a confluence point between outer harbor and inner harbor. The average depth of this channel is 10.7 m.
Station 3, is located in the centre of the **western arm** (WA, 0.88 km in length, 91 m in width and 10.7 m in depth) of the inner harbor. This is one of the three navigable arms of Visakhapatnam harbor.
Station 4, is located in the centre of the **northwestern arm** (NWA) of the inner harbor, which is the principal source of industrial effluents. A monsoon fed stream. 'Meghadrigedda' opens into this arm on the western side. The average depth of this arm is 10 meters.
Station 5, is located at the end of the **northern arm** (NA) which is the main commercial navigational channel of the inner harbor. The channel is about 152.4 m in width with an average of 10.7 m in depth.

A hired mechanized boat with no laboratory facilities was used for collection of samples. All photometric measurements were carried out on a Shimadzu Spectrophotometer (UV 260) using 1 or 5 cm path length cells. Particulate metals were analyzed on Orion Atomic Absorption Spectrophotometer after proper digestion.

Solvents like acetone, chemicals and acids used in the investigations were all of E-Merck analytical reagent grade. Double distilled water or de-ionized water was used in the estimation of trace metals and inorganic constituents except for ammonium ion for which ammonia free water was prepared by redistilling distilled water after treatment with potassium persulphate (1.5 g/L) and concentrated sulphuric acid (1 ml/L) was used. Particulate matter was collected separately on a total of 2 filters at each station and season, one is on 0.45 µm Membrane Millipore HA filter for total suspended particulate metals and other is on GF/F (0.7 µm) for chlorophylls. Millipore filtration apparatus was used for this purpose with a gentle vacuum. The volume of water that was filtered varied from 0.5 to 1.0 liters depending on the turbidity of the sample and its particulate content. All filters were washed with Milli Q water to remove salts and were kept frozen until further analysis.

Surface and bottom water samples were collected every month for a period of one year at five different stations in the harbor waters during the year 2012-2013 is shown in the figure 1.Surface waters were collectedwith a clean plastic bucket and bottom waters were collected Niskin bottom water sampler, they were immediately filtered through Glass fiber GF/F filters papers. The filtered waters are used for the determination of spatial and seasonal distribution of particulate trace metals like Cadmium and Copper in the harbor waters covering all the five stations during the year for all seasons.

III. Results And Discussion

1. Hydrography

The following hydrographic parameters were recorded / analysed during the entire period.

Temperature (°C):

The temperature was measured immediately after collection of both surface and bottom water samples with an accuracy of ± 0.1°C using or precision mercury thermometer.

pH :

pH of the sea water was measured immediately after the samples were brought to laboratory with an accuracy of ± 0.01 on Toshniwal digital (type-CL-46) pH meter using a combined calomel glass electrode. The instrument was calibrated with standard buffers of pH 4.00, 7.00 and 9.20 just before use.

Salinity (psu):

Almost all determinations of salinity today are based on the measurement of electrical conductivity for reasons of speed, accuracy and convenience. However, the earliest Mohr-Knudsen titrimetric method is still widely accepted by marine chemists. This method was adopted for determination of chlorinity in view of the limitation of facilities in the author's laboratory. The chlorinity values were converted to salinity values by the UNESCO equation, S % = 1.80655 x Cl ‰. The general principle of the method involves comparison of precipitable halides (Cl^- &Br^-) in the sample to those precipitated by silver ions from a standard sea water sample (Laboratoire Hydrographique Copenhagen). Halides present in an aliquot (10 ml) of sample were titrated with a solution of silver nitrate using potassium chromate as indicator. Silver nitrate solution was, in turn, standardized by standard sea water from the above equation and expressed in practical salinity scale (UNESCO, 1981). The salinities are represented assalinity practical units (psu).

Dissolved oxygen (DO. mg dm^{-3}) :

The dissolved oxygen content was determined by a modified Winkler's method (Carritt & Carpenter, 1966). The principle involved in this method 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 on board thus). In the presence of excess iodide, acidification leads to the liberation of an equivalent amount of tri iodide which can be titrated with standard thio sulphate using starch as an indicator.

2. Nutrients

Nitrite (NO^-_2, µM):

Determination of nitrite of nitrite in sea water is based on its reaction with an aromatic amine leading to the formation of diazonium compound followed by its coupling with an electron rich substrate usually a second aromatic amine to from an azo dye. The method adopted for the determination of nitrite in sea water in the present investigation was proposed by Bendschneier & Robinson (1952) and the modified method was given by Goldberg (1972). According to this method an aliquot of sea water sample was allowed to react with sulphanilamide in acid medium and the resulting diazonium ion was coupled with N (1-naphthyl) ethylene diamine dihydro chloride to give an intense pink dye. This method is very sensitive and is unaffected by the presence of other constituents normally present in sea water. The absorbance of the resulting pink solution was measured at 543 nm and the concentration of NO_2^- N in the sample was computed from a calibration curve.

Nitrate (NO_3-N, µM):

Estimation of nitrate in sea water is carried out in two stages. Nitrate present in the sea water is reduced to nitrite in the first stage and the resulting nitrite was determined as above by way of a pink azo dye in the second stage. Among several reducing agents available for this purpose, amalgamated cadmium is found to be the most efficient redactor of nitrate in sea water. The method described by Goldberg (1972) was followed for the fabrication and operation of the cadmium redactor column. The column efficiency (which was ~ 98% through out) was periodically tested with standard and samples collected through out the study period by subjecting all to the same treatment.

The procedure consisted in treating an aliquot (199 ml) of sea water sample with ammonium chloride buffer (2 ml) of 25% w/v) and passing the solution through an amalgamated cadmium redactor column. The eluent collected (25 ml), leaving initial and final eluents from the column was then treated with sulphanilamide and N (-1-naphthyl) ethylene diamine dihydro chloride and the absorbance of the resulting pink solution was measured photometrically at 543 nm against reagent blank (Morris and Riley, 1963; Grasshoff, 1964). The concentration of NO_3-N was computed from a calibration curve.

Ammonia (NH_3 + NH_4, µM):

Of the various photometric procedures available for the determination of ammonia in sea water, indophenol blue method (Koroleff, 1969) is the most satisfactory one, because of its reproducibility, low reagent blank and freedom from interference by organic nitrogen compounds. The method basically consists of formation of monochloramine by the reaction of ammonia with trion (1,3-dichloro-cyanuric acid) which on reduction with phenol in alkaline medium gives an intensify coloured indophenol blue. Trisodium citrate is used as a comprising agent for Ca and Mg to prevent them from precipitation, under the high pH conditions of the reaction. The absorbance of the resulting blue solution is then measured at 630 nm against reagent blank and the concentration of ammonia-N computed from a calibration curve.

Orthophosphate (µM):

All the methods involved for the determination of dissolved inorganic phosphorus of sea water are based on the reaction of phosphate with acidified ammonium molybdate reagent to yield a phosphor-molybdenum complex, which when reduced gives a coloured molybdenum blue complex. Among the various reducing agents employed, ascorbic acid is found to be more effective and convenient. The method adopted in the present investigation is a modified procedure of Murphy & Riley (1962) as cited by Goldbirg (1972). According to this method, a mixed reagent containing sulphuric acid, ammonium molybdate and antimonyl tartarate and a second ascorbic acid reagent are separately prepared. The absorbance of the resulting blue coloured solution is measured photometrically at 880 nm against a reagent blank. The concentration of orthophosphate is computed from a calibration curve. Major cations and anions in sea water and elements like silicon, arsenic etc., which are capable of forming heteropoly acids with molybdate ion do not interfere with the reaction under these conditions.

Chlorophyll-a (mg.m^3)

Phytoplankton's are mostly uni-cellular algae endowed with certain pigments like chlorophylls, pheo-pigments and carotenoids etc. Two methods, one based on fluorimetry and the other on spectrophotometry are available for their determination in acetone extracts. In the present investigation, the latter was used, which in turn could in principle be applied through different sets of equations like those proposed by Strickland and Parsons (1963), UNESCO, (1966) and Richards & Thomson (1952). The GF/C filter containing particulate matter mentioned earlier was transferred to a graduated stoppered test tube and extracted with 10 ml of 90% acetone and then kept in a refrigerator for 24 hours. The absorbance of the clear acetone extract was measured photometrically using 1 or 5 cm cells against reagent blank at different wave lengths (750, 664, 630, 510 and 480 nm). Concentrations of chlorophyll-a was then calculated using the equation of Strickland & Parsons (1972)

IV. FIGURES AND TABLES

FIG 2.1 VISAKHAPATNAM HARBOUR AND STATION LOCATIONS (St. 1-St. 5)

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