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Dissolved Methane Fluctuations in Relation to Hydrochemical Parameters in Tapi Estuary, Gulf of Cambay, India

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ABSTRACT: Methane is one of the important greenhouse gases that contribute to a rise in global mean surface temperature. Aquatic environments are postulated to contribute > 50% of the total global methane (CH_4) flux to the atmosphere (de angelis and Lilley, 1987). Dissolved methane concentration in surface waters was measured from January to December 2008 at two selected sites upper reaches (ONGC Bridge) and lower reaches (Dumas) of Tapi estuary, Gulf of Cambay, Gujarat, India. Besides, the important hydrochemical parameters like total organic carbon (TOC), dissolved oxygen (DO), salinity and nutrients (phosphate, nitrate and sulphate) were also analyzed. The mean dissolved CH_4 concentration for all water samples at upper reaches was 1369.00 nmol/L and at lower reaches was 1082.04 nmol/L. The positive correlation was found between dissolved methane content and total organic carbon. On the contrary, the negative correlation was observed between methane concentration and nutrients like dissolved oxygen, salinity, phosphate, nitrate and sulphate. The probable causes for varying dissolved methane concentration and saturation at different reaches with hydrochemical parameters are discussed.

Key words: Dissolved CH_4, Tropical estuary, Total organic carbon and nutrients

INTRODUCTION

Methane is an atmospheric trace gas that contributes significantly to the greenhouse effect. Despite its lower concentrations in the atmosphere, CH4 absorbs infrared radiation much more intensely than CO2 and contributes about 15% to the anthropogenic greenhouse effect (Ferron *et al.*, 2007). Many investigations have been carried out to control methane for various purposes but little attention is given to aquatic systems (Banu *et al.*, 2007; Zinatizadeh *et al.*, 2007; Yoochatchaval *et al.*, 2008; Uemura, 2010). Most investigations on methane emissions from aquatic ecosystems have concentrated on salt marshes (Cicerone and Shetter, 1981). Oceans play only a modest role in methane global budget, accounting for 0.1% to 4% of the total atmospheric emissions (Crutzen, 1991). These oceanic emissions of CH_4 are not homogeneously distributed. Hence, biological productive regions, such as estuaries and coastal areas contribute about 75% to the global oceanic CH_4 production (Bange *et al.*, 1994). Due to the shallowness of the estuarine systems, a large fraction of labile organic matter can be deposited in the sediments which generate favorable conditions for the microbial production of methane (Bange *et al.*, 1998). Biogenic methane is produced exclusively by a group of strict anaerobes (methanogens) during methanogenesis. This process occurs in the sediments, in the interior of suspended particles and in the guts of marine organisms (Wolfe, 1971). The actual methane concentration at any point is a complex function of many factors including hydrology, drainage basin morphology and vegetation, microbial oxidation, and reaeration. Hydro-geochemistry of the wetlands and paddy fields influences the methane emission (Nirmal Kumar and Viyol, 2008 and 2009). Methane concentration of mangrove forest sediments were investigated with respect to organic matter content, bacterial numbers and sulphide concentration

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and redox potential profiles (Lyimo *et al.*, 2002). Methane and suspended particulate matter (SPM) concentrations in the tidal regions of the Garonne and Dordogne rivers were studied by Abril et al (2007). In this paper, we present for the first time, the seasonal fluctuations of dissolved CH_4 and saturation point and its relation with hydro-chemical nutrient concentrations at two sites of tropical Tapi estuary, Gujarat, India.

The area of study is Tapi Estuary; a shallow and wide segment exhibits characteristics of a typical estuary in the Gulf of Cambay ,South West of Gujarat (21°402 N, 72° 402 E). It is characterized by semi-diurnal tides (average tidal range 2.3–5.5 m, 25 km upstream during spring tide and 0.4 - 2.3 m, during neap tide). The water column is well mixed except during short period of tidal cycle (Qasim, 2003). The system receives the inputs of organic matter and nutrients coming from the domestic wastewater discharges from Surat City, a textile hub located in the upper reaches part of the estuary. Furthermore, the lower part of Tapi estuary receives the drainage of domestic sewage from Dumas as well as industrial effluent from Hazira, a major industrial complex of Gujarat, India. This industrial area includes ONGC, Reliance petrochemical, KRIBHCO, NTPC, L & T, ESSAR steel etc. Two sites were selected for the present study namely ONGC Bridge upper reaches and Dumas lower reaches (Fig.1).

MATERIALS & METHODS

Between January and December, 2008, monthly sampling collections were performed at two fixed station namely ONGC Bridge and Dumas in Tapi estuary during third week of every month. In each sampling, surface water samples were also drawn in 300 mL airtight glass bottles, preserved with saturated mercuric chloride to inhibit microbial activity and sealed with grease to prevent gas exchange. They were stored in the dark until analysis in the laboratory within a day or two after the collection. Surface water samples for hydro-chemical properties were also collected separately in wide mouth inert polyethylene bottle during each sampling. While surface water sample for Dissolved

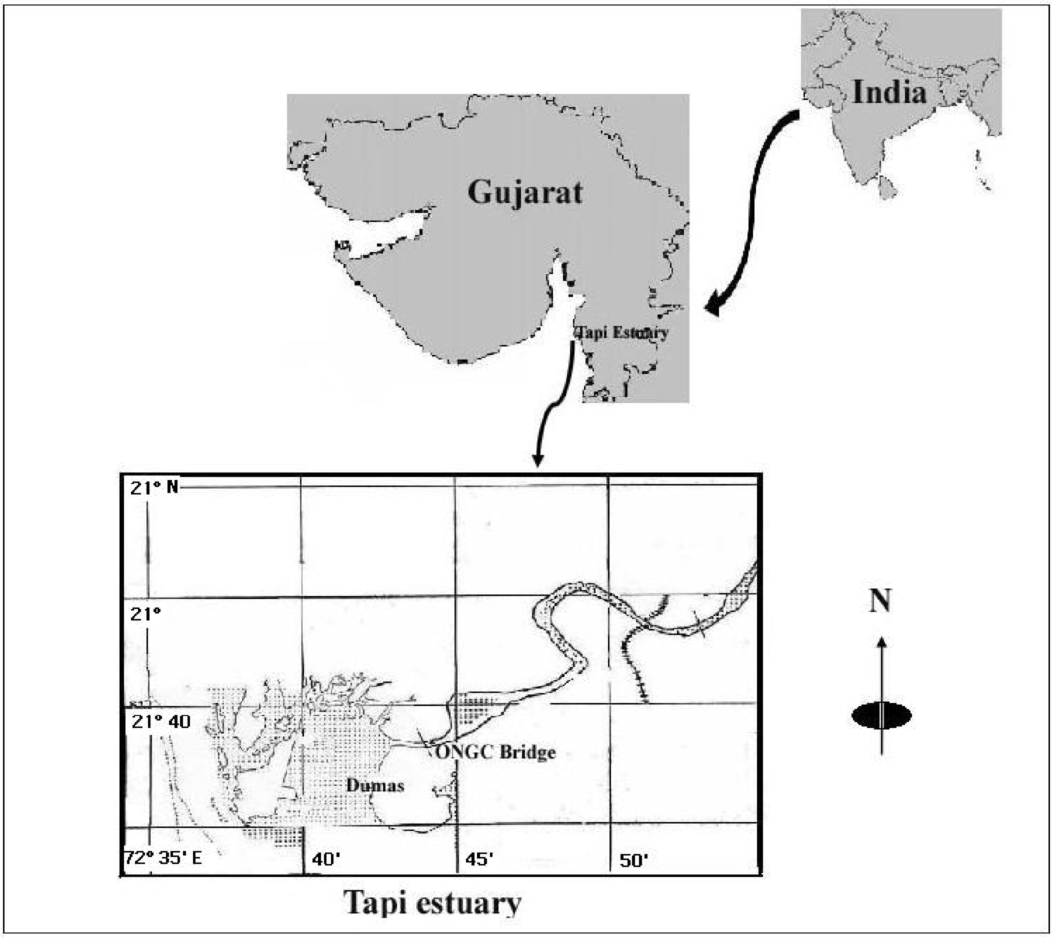


Fig. 1. Selected sites of Tapi estuary

Oxygen (DO) content was collected in 300 mL DO glass bottle without any air bubbling to avoid gas transfer from the atmosphere and fixed and analyzed on site by Winkler titration (APHA, 1998). Simultaneously temperature of the surface water was also recorded.

Dissolved CH_4 concentration was determined by gas chromatography. A head space technique was employed to extract dissolved CH_4 from the water sample. A predetermined volume (approximately 25 mL) was equilibrated with an ultra pure N_2 in a 50 mL air-tight glass syringe equipped with 3-way polycarbonate stopcocks. Equilibration was achieved by vigorous shaking of syringe at room temperature (Jayakumar *et al.,* 2001). After equilibrium, a sample of the head space was injected into a gas chromatograph (Perkin Elmer Auto system XL). Nitrogen is used as the carrier gas (30 mL/min A flame ionization detector (FID), operated at 300 °C, is used to measure CH_4. Temperature setting was 100 °C, 45 °C and 150 °C for oven, column and detector, respectively. The detector was calibrated daily using CH_4 standard (5ppmv ± 0.1), made and certified by UPL Gas Suppliers, India. The concentration of CH_4 in the water samples were calculated from the concentrations measured in the head space, using the functions for the Bunsen solubilities given by Wiesenburg and Guinasso (1979). Saturation values were calculated using formula (Ferron *et al.,* 2007) and expressed in % values:
% saturation = (measured concentration / expected equilibrium concentration) x100

Total organic carbon (TOC) in surface water samples was measured using total organic carbon analyzer (Shimadzu, TOC-VCSN) by catalytically aided combustion oxidation at 680°C. Salinity was determined by Mohr–Knudsen titration and standardized with standard of (chlorinity, Cl=19.374‰). Briefly, the methods used for the analyses for nutrients were: Dissolved phosphate (PO_4) was measured by the phosphomolybdenum blue method using molybdate blue and ascorbic acid. Whereas, Nitrite + Nitrate (NO_2+NO_3) were determined by the sulphanilamide and N (1-napthyl) ethylenediamine method after cadmium reduction of nitrate to nitrite (Grasshoff *et al.,* 1983 and APHA, 1998). All the parameters were analyzed within 24-48 hrs after sampling. Correlation analysis between parameters and one-way Analysis of Variance (ANOVA) were employed for the data set.

RESULTS & DISCUSSION

The mean dissolved CH_4 concentration for all samples at ONGC Bridge was 1369.00 nmol/Land at Dumas was 1082.04 nmol/L (Fig. 2 a). Moreover, monthly variations are well distinct that shooted up during monsoon and pre-monsson months than that of winter months. Dissolved methane concentration exhibited increasing trend with the months and found higher in the pre monsoon months at both the sites. The higher dissolved methane values registered at the upper reaches ONGC Bridge than the lower reaches Dumas could be due to uninterrupted tides leading to non- mixing processes, freshwater inputs and addition and deposition of municipal wastes. However, tidal dilution at lower reaches occurs more readily, which might be possible reason for the linear methane concentration at Dumas. Similar trend of declination of methane concentrations from fresh to salt water (lower reaches) was observed by Jayakumar et al (2001) in coastal and offshore waters of the Arabian Sea. Methane saturations was observed in the range of 23, 505-1, 91,308 % and 10,614-1, 65,008% for ONGC Bridge and Dumas, respectively (Fig. 2 b). Similar observations were made by Middelburg et al. (2002) and noticed saturation up to 1, 58,000% in European tidal estuaries (Elbe, Ems, Thames, Rhine, Scheldt, Loire, Gironde, Douro, Sado). However, higher methane concentration and corresponding saturation was registered in monsoon and post monsoon months. This might be due to higher loading of organic matter and nutrients from the effluent and runoff, higher residence time because of tidal regime, which may provide favorable conditions for CH_4 production.

Surface water temperature was fluctuated in the range of 25 °C in November to 32.2°C in June at Dumas (Fig. 2 c). Dissolved Oxygen concentration showed distinct seasonal variation (Fig. 2 d) with the range of 1.68 mL/l in May to 9.55 mL/ l in Nov at ONGC Bridge. Temperature showed positive correlation with methane concentration. Higher temperature accelerated the methanogens activity might be reason (Dubey, 2005). Salinity in the estuary was registered in the range of 1.72 ppt at ONGC in July to 26.89 ppt at Dumas in January (Fig. 2 e). Present investigation reveals that the correlation between salinity and dissolved CH_4 (r^2 = "0.31 and "0.46 for ONGC Bridge and Dumas, respectively) was found to be weak and negative. Similar linear negative correlation of estuarine CH_4 concentrations with increasing salinity was observed by Middelburg *et al.* (2002) in temperate estuaries. There was an inverse correlation (r^2= "0.68 and -0.06) between dissolved O_2 to CH_4, similar to that observed between CH_4 and salinity. The possible reason might be a reduction in CH_4 oxidation, which could occur due to lower dissolved O_2 levels (Shalini *et al.,* 2006).

Total organic carbon in surface water fluctuated in the range of 8.78 mg l^{-1} in July to 39.09 mg l^{-1} in June at Dumas (Fig. 2 f). However, TOC was found greater at upper reaches than the lower reaches. The linear correlation between TOC and dissolved methane was found to be positive (r^2=0.33 and 0.36 for ONGC Bridge and Dumas, respectively). The high loading of organic matter provides favorable conditions for the production of CH_4 (Ferron *et al.*, 2007).

Phosphate values varied in the range from 0.40 µmol l^{-1} at upper estuary (ONGC Bridge) in August to 4.43 µmol l^{-1} at lower estuary (Dumas) in April. In contrast to phosphate, nitrate was found greater in the upper estuary (ONGC Bridge) than in the lower estuary (Dumas) (Fig. 2.g and h). Both phosphate and nitrate content showed weak or negative correlation with methane content (Kang and Freeman, 2004). Dissolved sulphate was observed in the range of 0.98 in August at ONGC Bridge to 3.23 mmol l^{-1} in April at Dumas. However, sulphate content was found higher at lower reaches than in upper reaches. Dissolved CH_4 showed a negative correlation with dissolved sulphate (r^2=”0.13). High Sulphate content inhibits the methanogenesis which in turn reduces CH_4 production in marine sediments (Dubey 2005) could be the reason in present study. Seasonally methane concentration was increased in monsoon months and post monsoon months but declines with the onset of the winter at both the sites. The greater input of organic matter with fresh water and higher suspended solid

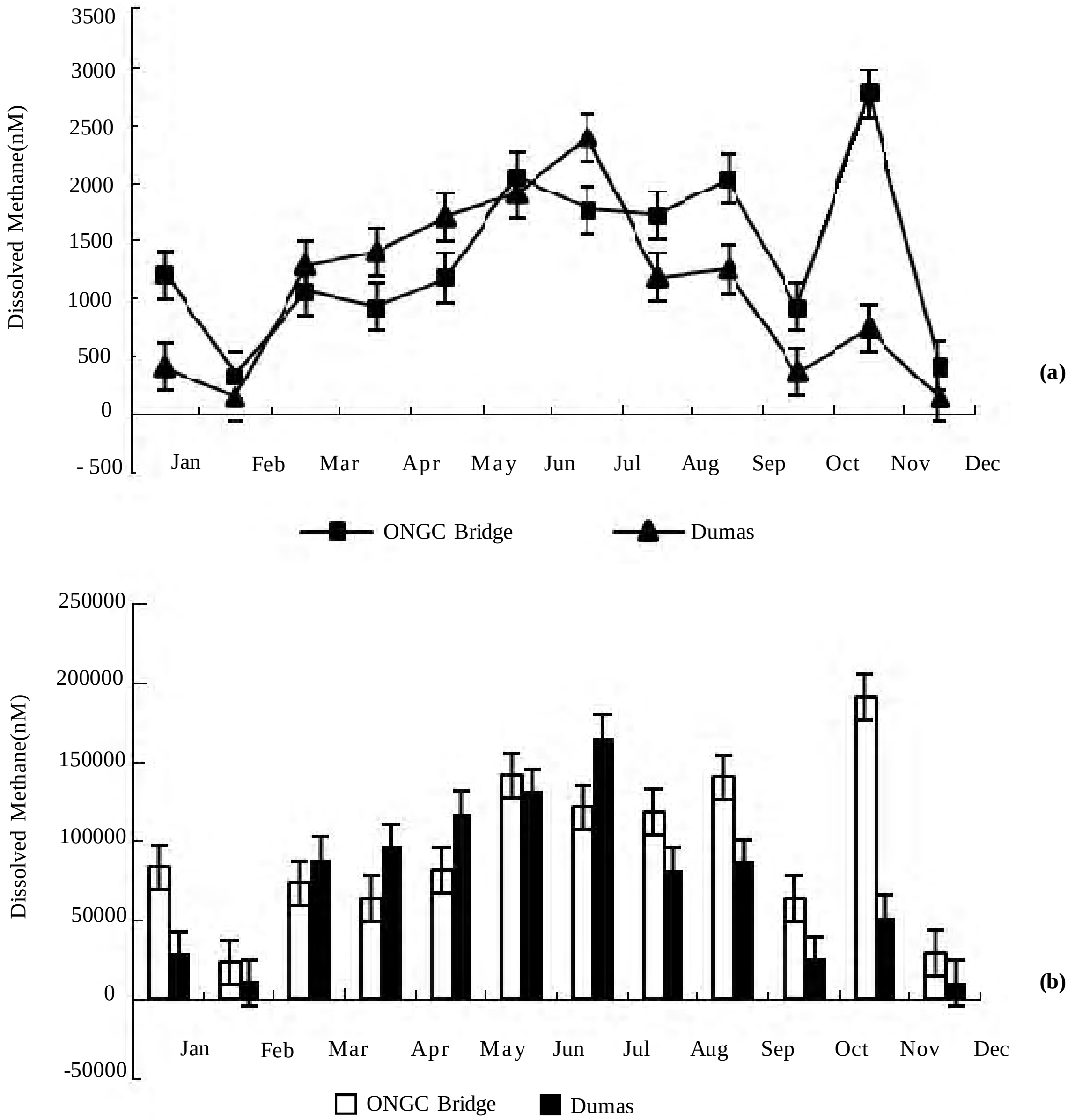
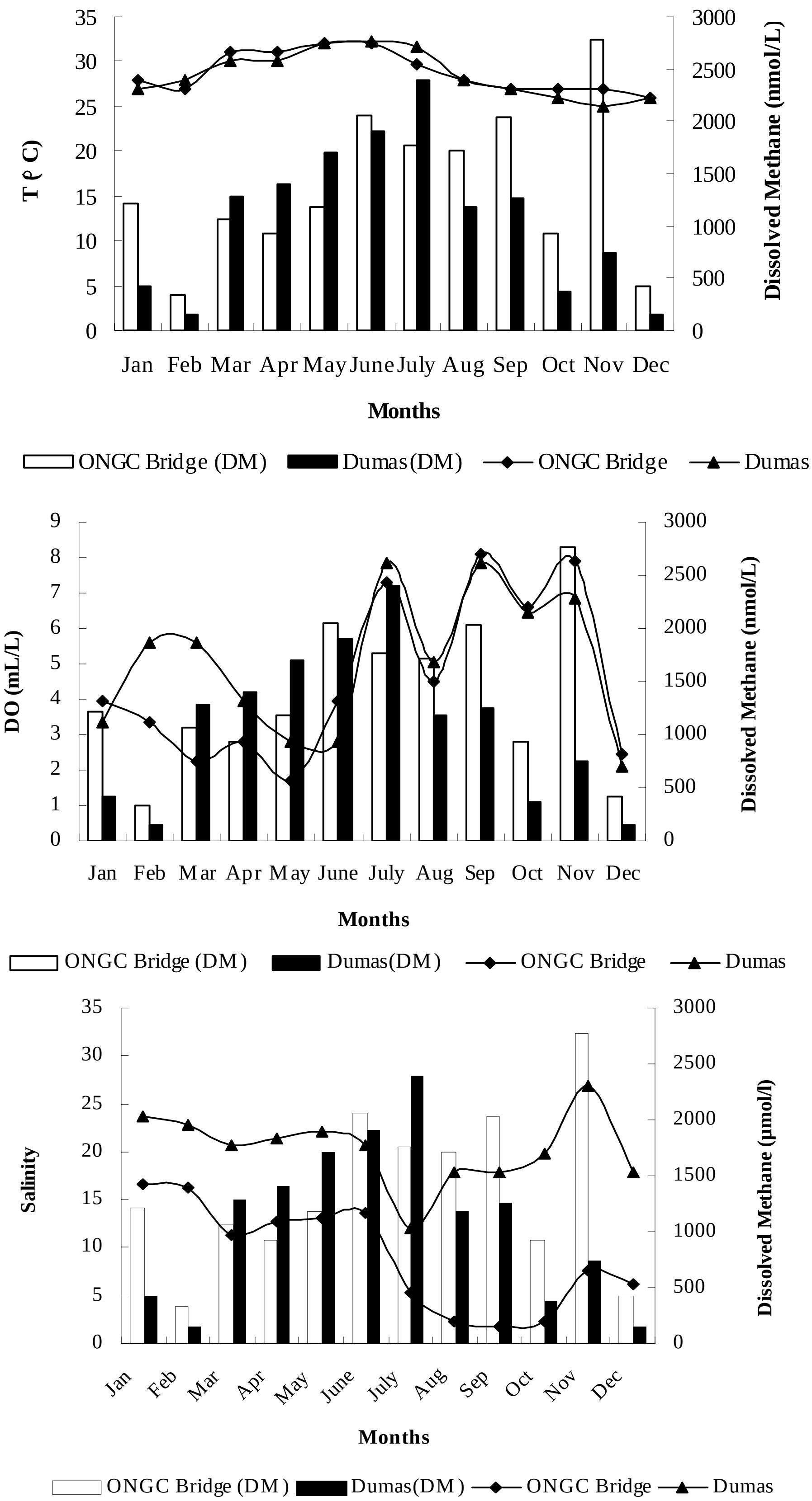


Fig. 2. showing (A) Dissolved methane (B) Methane saturation (C) Temperature and dissolved CH_4 concentration (D) Dissolved oxygen and dissolved CH_4 concentration (E) Salinity and dissolved CH_4 concentration (F) Total organic carbon and dissolved CH_4 concentration at both the sites (G) Nutrients and dissolved CH_4 concentration at ONGC Bridge (H) Nutrients and Methane concentration at Dumas(Continues)



(c)

(d)

(e)

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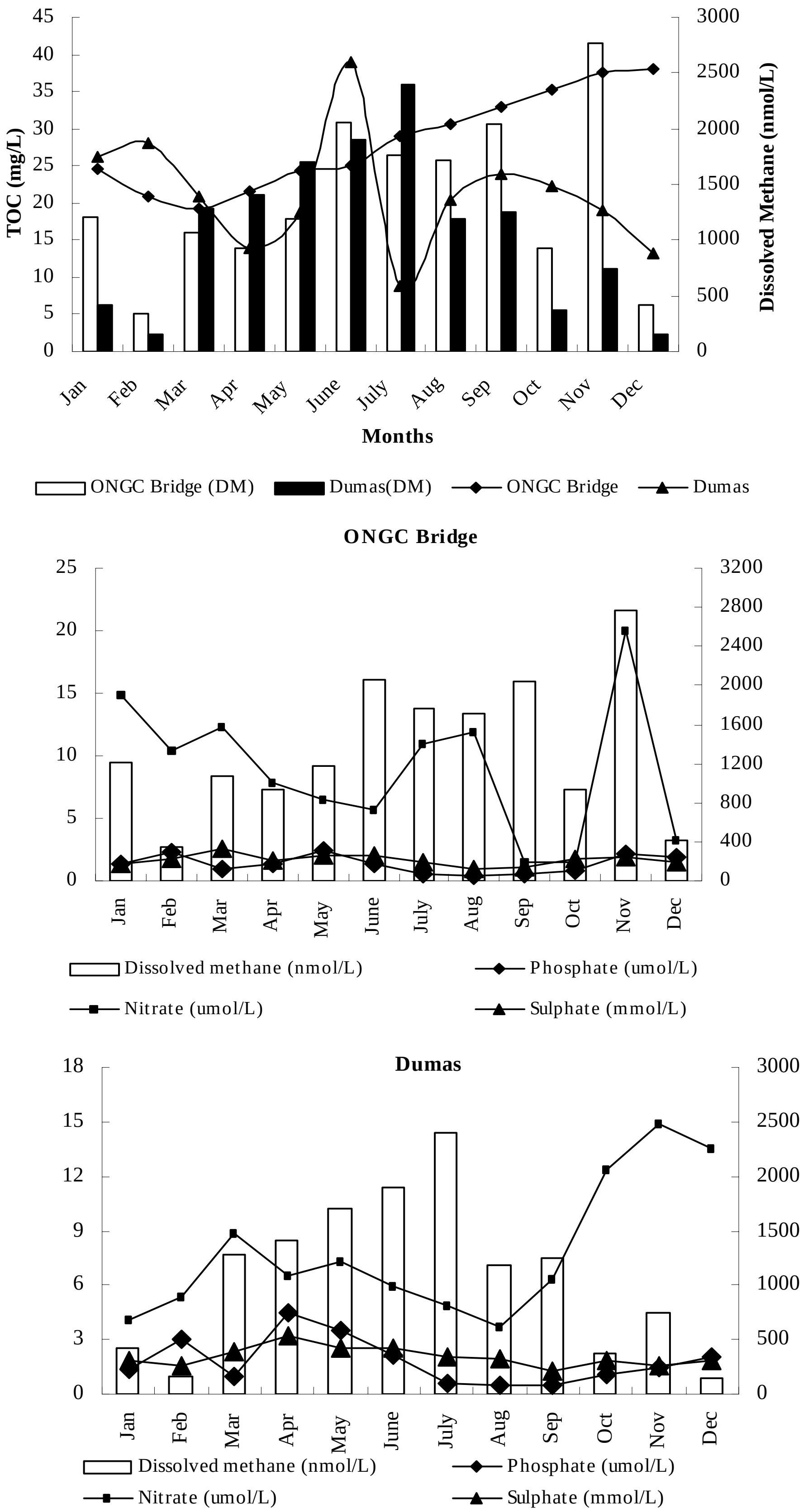

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(g)

(h)

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due to turbulence run-off rain water flow may be the responsible. In monsoon months methane concentration and other parameters were higher at the lower reaches than the higher reaches. This might be due to greater input of the organic load than the lower reaches from the Surat city (Lane 2002). One way ANOVA showed slight variation ($p = 0.15$) in dissolved methane concentration between ONGC Bridge and Dumas.

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REFERENCES

Abril, G., Commarie, M. V. and Guerin, F. (2007). Enhanced methane oxidation in an estuarine turbidity maximum. Limnol. Oceanogr., **52 (1),** 470-475.

APHA (1998). Standard methods for examination of water and waste water. Washington D.C., American Public Health Association, USA.

Bange, H. W., Bartel, U. H., Rapsomanikis, S. and Andreae, M. O. (1994). Methane in the Baltic and North Seas and reassessment of the marine emissions of methane. Glob. Biogeochem. Cycles., **8**,465-480.

Bange, H. W., Dahlke, S., Ramesh, R., Meyer-Reil, L.A., Rapsomanikis, S. and Andreae, M. O. (1998). Seasonal study of methane and nitrous oxide in the coastal waters of the southern Baltic Sea. Estua. Coast. Shelf Sci., **47**, 807–817.

Banu, J. R., Kaliappan, S. and Yeom, I. T. (2007). Treatment of domestic wastewater using upflow anaerobic sludge blanket reactor. Int. J. Environ. Sci. Tech., **4 (3)**, 363-370.

Cicerone, R. J. and Shetter. J. D. (1981). Sources of atmospheric methane: Measurements in rice paddies and a discussion. J. Geophy. Res., **86**, 7203-7209.

Crutzen, P.J., (1991). Methane's sinks and sources. Nature. **350**, 380-381.

de Angelis, M. A. and Lilley, M. D. (1987). Methane in surface waters of Oregon estuaries and rivers. Limnol. Oceanogr., **32 (3)**, 716-722.

Dubey, S. K. (2005). Microbial ecology of methane emission in rice agroecosystem- A Review. App. Eco. & Environ. Rese., **3 (2),** 1-27.

Ferron, S., Ortega, T., Gomez-Parra, A. and Forja, J. M. (2007). Seasonal study of dissolved CH_4, CO_2 and N_2O in a shallow tidal system of the bay of Cadiz (SW Spain). J. Mar. Sys., **66**, 244-257.

Grasshoff, K., Ehrhardt, M. and Kremling, K. (1983). Methods of seawater analysis. Verlag Chemie, Berlin.

Jayakumar, D. A., Naqvi, S. W. A., Narvekar, P. V. and George, M. D. (2001). Methane in coastal and offshore waters of the Arabian Sea. Mar. Chem., **74 (1),** 1-13.

Lane, R., Day, W. J., Marx, B., Reyes, E. and Kemp, P. (2002). Seasonal and Spatial Water Quality Changes in the Outflow Plume of the Atchafalaya River, Louisiana, USA. Estuaries, **25 (1)**, 30–42.

Lyimo, T. J., Arjan, P. and Opden Camp, H. J. M. (2002). Methane Emission, Sulphide Concentration and Redox Potential Profiles in Mtoni Mangrove Sediment, Tanzania Western Indian Ocean. J. Mar. Sci., **1 (1),** 71–80.

Middelburg, J. J., Nieuwenhuize, J., Iversen, N., Hoegh, N., de Wilde, H., Helder, W., Seifert, R. and Christ, O. (2002). Methane distribution in European tidal estuaries. Biogeochemistry, **59,** 95–119.

Nirmal Kumar, J. I. and Viyol, S. (2008). Short term assessment of influence of hydro-geochemistry on methane emission from two contrasting tropical wetlands of Central Gujarat, India. Int. J. Nat. Env. and Poll. Tech., **7 (1),** 15-20.

Nirmal Kumar, J. I. and Viyol, S. (2009). Short term diurnal and temporal measurement of methane emission in relation to Organic carbon, Phosphate and sulphate content of two rice fields of central Gujarat, India. Paddy and Water Environment,**7**, 11-16.

Qasim, S. Z. (2003). Indian estuaries. Allied publishers, 356-357, India.

Shalini A, Ramesh, R. Purvaja R. and Barnes J. (2006). Spatial and temporal distribution of methane in an extensive shallow estuary, south India. J. Earth Sys. and Sci., **115 (4),** 451-460.

Uemura, Sh. (2010). Mineral Requirements for Mesophilic and Thermophilic Anaerobic Digestion of Organic Solid Waste. Int. J. Environ. Res., **4 (1)**, 33-40.

Wiesenburg, D. A. and Guinasso Jr., N. L. (1979). Equilibrium solubilities of methane, carbon monoxide, and hydrogen in water and sea water. J. Chem. Eng. Data, **24**, 356-360.

Wolfe, R.S. (1971). Microbial formation of methane. Adv. Micro. Phys., **6,** 107–146.

Yoochatchaval, W., Ohashi, A., Harada, H., Yamaguchi, T. and Syutsubo, K. (2008). Intermittent Effluent Recirculation for the Efficient Treatment ofLow Strength Wastewater by an EGSB Reactor. Int. J. Environ. Res., **2 (3)**, 231-238.

Zinatizadeh, A. A. L., Salamatinia, B., Zinatizadeh, S. L., Mohamed, A. R. and Hasnain Isa, M. (2007). Palm oil mill effluent digestion in an up-flow anaerobic sludge fixed film bioreactor. Int. J. Environ. Res., **1(3)**, 264-271.