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SHORT TERM ASSESSMENT OF INFLUENCE OF HYDROGEOCHEMISTRY ON METHANE EMISSION FROM TWO CONTRASTING TROPICAL WETLANDS OF CENTRAL GUJARAT, INDIA

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ABSTRACT

Methane emission from two wetlands namely Khodiyar and Pariyej of Central Gujarat, India was measured during pre-summer season. Along with the methane emission, hydro and geo chemistry of these two contrasting wetlands $(SO_4^{2^2}, PO_4^{-2} \text{ and organic carbon})$ were determined. The methane emission ranged from 1219.51 mg/m²/h to 7274.47 mg/m²/h, having greater emission at noon period (11 am to 1 pm) of the day in the Khodiyar wetland. Besides, the methane emission ranged between 80.84 mg/m²/h and 495 mg/m²/h, having higher emission at same time of the day at Pariyej wetland. The methane release was declined from first trip followed by second, third and fourth trips. The results of the current investigation confirm that hydrochemistry and geochemistry might control methane emission in both the wetlands. Correlation analysis revealed that the methane emission from both the sites has positive correlation with organic carbon of the sediment and negative correlations with phosphate and sulphate content of water and sediment. The details of the reasons have been discussed in this paper.

INTRODUCTION

Methane is considered as one of the most important greenhouse gases in the atmosphere and contributes 15-20 % to the global warming (IPCC 1996). Methane is emitted from a variety of both humanrelated (anthropogenic) and natural sources or activities. Human-related activities include fossil fuel production, animal husbandry (enteric fermentation in livestock and manure management), rice cultivation, biomass burning and waste management. Natural sources of methane include wetlands, gas hydrates, permafrost, termites, oceans, freshwater bodies, non-wetland soils and other sources such as wildfires. A recent survey of sources of atmospheric methane in New England suggests that as much as 36% of methane release to the atmosphere may be from wetlands (Blaha et al. 1999). Moreover, natural wetlands play a disproportionately large role in CH₄ emissions. Wetlands are likely the largest natural sources of CH₄ to the atmosphere, accounting for about 20% of the current global annual emission. Out of the total amount of CH₄ emitted, northern wetlands contribute 34%, temperate wetlands 5%, and tropical systems about 60%. Eight of the controlling factors, including carbon supply, soil oxidation-reduction status, pH, temperature, vegetation, salinity and sulphate content, soil hydrological conditions and CH₄ oxidation have been discussed by Wang et al. (1996).

Because of the strict anaerobic conditions required by CH_4 -generating microorganisms, natural wetland ecosystems are one of the main sources of biogenic CH_4 . The production of methane is also dependent on the presence of anaerobic conditions, fermentable organic matter, and methanogenic bacteria. Many environmental conditions are known to impact the rate of methane production including temperature, the presence of alternative electron acceptors and pH. The rate of release is controlled by the rate of production, the rate of consumption (primarily as methane oxidation), and the mechanisms of transport (primarily diffusion, gas bubble ebullition and transport through plants (Duval & Goodwin 2000). The methane emission registered two peaks during spring and early

summer (Kang & Freeman 2004). So, it is important to understand the characteristics and properties of methane emission from the wetlands during early summer. So far no attempts have been carried out in the State of Gujarat on these lines. The purpose of this study is to explore short term diurnal and temporal release of methane and to correlate the methane emission with organic carbon, sulphate and phosphate content of water and sediment from two wetlands in Anand district of central Gujarat.

MATERIALS AND METHODS

The study was carried out in two wetlands of Anand district of central Gujarat to study the diurnal as well as temporal variation of methane fluxes in relation to the hydrogeo chemistry and other environmental factors. Both the wetlands are contrasting in nature and composition of biota, and remain unidentical in all respects. Both the wetlands were differing in morphometry, nature sources, biotic and abiotic components, i.e., Khodiyar wetland is sewage fed whereas Pariyej wetland is freshwater community reservoir.

Descriptions of Sites

Khodiyar wetland: Sewage and domestic wastewaters of Anand and Vallabh Vidyanagar township accumulated at one place and formed this permanent wetland. It is shallow, highly organically polluted pond, having a depth of 2-4 feet and situated 5-8 km away from Anand town fringing its northern boundary. However, this wetland is supported by abundant growth of aquatic vegetation e.g., *Eichhornia crassipes, Hydrilla verticillata, Typha latifolia*, etc. and good number of aquatic birds, i.e., 40,000 to 50,000 like Greater Flamingo, Lesser Flamingo, Spot-billed duck, Greylag Goose, Spoonbill, Storks, Sarus crane, etc. Every winter thousands of birds migrate to this wetland, which could be a good source of their shelter as well as feeding refuge.

Pariyej wetland: Pariyej is situated about 45 km from Anand on 22° 33' N latitude and 72° 38' E longitude at an altitude of 13 to 14 m above mean sea level, covering an area of 500 ha. It falls under 4-B Gujarat Rajwara region of central Gujarat, and is an important natural water storage reservoir. It lies in a permanent, natural depression, surrounded by embankment with a circumference of about 9 km. This wetland is surrounded by five villages and villagers are dependent on this wetland for food, fodder and economy. Climate of the region is dry tropical monsoon type with an average annual rainfall of about 800 mm concentrated in July, August and September. It harbours an abundant growth of aquatic vegetation e.g., *Ipomoea aquatica, Marseilia quadrifolia, Nelumbo officinalis, Nymphea stellata* and profuse beds of *Typha anugstifolia* along the banks. Besides, it also harbours resident birds like Sarus cranes, Egrets, Lapwings, Storks; the main chunk of migratory birds comprise Flamingos, Sandpipers and Coots that fly in from China during winter. This wetland also supports a small fishery.

Methane Emission Measurement

Methane emission was measured by static chamber technique followed by the method of Duchemin et al. (1999). An area of approximately 1 m^2 was enclosed by a chamber in order to rise and collect the concentration of the gas emitted. The static chamber made up of transparent plastic was placed in the littoral zone of the wetland. The lower edge of the chamber was dipped inside the water to avoid the gas leakage. Chamber was provided with two permanent gas releasing taps on its both the sides. Gas samples were drawn from the chambers using rubber air bladders. Then the gas samples were sucked by syringe equipped with three-way cock, into an evacuated sealed vial. Vials were sealed with self-closing rubber septum. After taking gas sample, the chamber was evacuated using air bladders (Fig. 1).

16

The methane gas was collected early in the morning at 9:00 a.m. and repeated every two hour interval up to 5 pm to study the diurnal methane emission fluctuation. Gas samples were collected every 15 days from end of February to April, 2007 to study temporal variation. Immediately after collection of methane the gas samples were transported to the laboratory at normal pressure. Methane gas concentration was determined by Perkin Elmer Autosystem Gas Chromatograph equipped with FID (Flame Ionization Detector) in Sophisticated Instrumentation Centre for Applied Research and Testing (SICART), V. V. Nagar, Gujarat. The temperature settings administered were 60°C, 110°C and 150°C for column, injector and detector of GC, respectively. The calculations for methane gas have been made by the following formula and gas concentration is represented in mg/m²/h.



Fig 1. Collection of methane using gas chamber with two cocks connected to gas bladder.

Calculation of Methane Emission

Methane emission $(mg/m^2/h) = [(Ps*Cs)/P_{std})*V_v/V_a)*V_h]/(A*H)$

Where,

Ps = Peak area for sample in gas chromatograph

Cs = Concentration of the standard methane gas (mg/L)

 $P_{std} = Peak$ area for standard in gas chromatograph

 V_{u}^{su} = Volume of the vial (mL)

 $V_{a} = Volume of air sampled (mL)$

 $V_{\rm b}$ = Volume of head space of the chamber, i.e. [length*breadth*height of the chamber] (l)

A = Area covered by the chamber (m²)

H = Enclosure period (h)

Water and Sediment Collection and Analysis

Water and sediment samples were collected simultaneously at two hours intervals from all the sites along with the time of gas sampling. Water samples were stored in plastic bottles. Sediment samples were collected with the help of spade and stored in plastic bags. Both, water and sediment samples were transferred to the laboratory and subjected to chemical analysis such as organic carbon of sediments, sulphate and phosphate content of water and sediments using the standard methodology of Trivedy et al. (1987) and Maiti (2003). The experimental data were analysed statistically for simple correlation coefficient (r) and ANOVA.

RESULTS AND DISCUSSION

Methane emission from the Khodiyar wetland was found in the range of 1219.51 mg/m²/h to 7274.47 mg/m²/h. (Fig. 2A). The maximum flux was found during first trip of the exposure period, i.e., 11.00 a.m. to 1.00 p.m. The lowest emission was observed during the fourth trip but higher emission was observed at third exposure period, i.e., 11.00 a.m. to 1.00 p.m. Methane emission from the Pariyej wetland ranged between 80.84 mg/m²/h and 495 mg/m²/h. The maximum emission was found during the first trip between 11.00 a.m. to 1.00 p.m. (Fig.2B). The lowest emission was achieved during the fourth trip between 9.00 a.m. to 11.00 a.m. to 1.00 p.m. which is very well coincided with the findings of Juutinen (2004) that diurnal variation flux of CH₄ was regular, large and had a distinctive pattern with the daily maximum occurring around noon.



Fig. 2: Diurnal fluctuation of methane emission content from Khodiyar wetland (A) and Pariyej wetland (B).



Fig. 3: Average value of organic carbon and methane emission content from Khodiyar wetland (A) and Pariyej wetland(B).



Fig. 4:Average value of phosphate and sulphate content of water and methane emission Khodiyar wetland (A) and Pariyej wetland (B).



Fig. 5: Average value of phosphate and sulphate content of sediment and methane emission Khodiyar wetland (A) and Pariyej wetland (B).

It has been experienced in the present investigation that methane emission was declined from first trip followed by second, third and fourth trips from February to April, 2007, which might be due to decline of water level, increase in high temperature and light intensity during the successive trips due to onset of summer season. These results corroborated the observations of Smith et al. (2000), with the view that methane was emitted in all the temporarily flooded plots during the inundation, but after drying the fluxes decreased to very low levels and the driest sites even turned to sinks of atmospheric CH_4 .

Moreover, organic carbon content of the sediments also exhibited similar diurnal pattern with the methane flux, and was observed in the range from 0.06 to 0.32%. It recorded greater value during first trip followed by second, third and fourth from Khodiyar wetland (Fig 3A). Organic carbon content of the sediment was found in the range of 0.01 to 0.07 % from Pariyej wetland. It was also recorded greater in concentration during first trip followed by second, third and fourth (Fig 3B). Verma et al. (2002) observed that sediment organic carbon controls the rate of methane release while studying the methane emission from the Vembanad lake.

However, the methane release from both the wetlands was greatly influenced by phosphate and sulphate content of the water and sediment. Phosphate and sulphate content of water ranged from 59 to 113 mg/L and 0.1 to 4.69 mg/L, respectively at Khodiyar wetland (Fig 4A), while phosphate and sulphate contents of water ranged from 3 to 80 mg/L and 0.1 to 7.86 mg/L, respectively at Pariyej wetland (Fig 4B). On the other hand phosphate and sulphate contents of sediment ranged from 0.01 mg/g to 0.87 mg/g and 27 mg/g to 65 mg/g, respectively for the Khodiyar wetland (Fig. 5A). Maximum and minimum values of phosphate and sulphate contents of sediments showed 0.06 mg/g to 0.11 mg/g and 3 mg/g to 9 mg/g, respectively for Pariyej wetland (Fig 5B). The rate of methane release, organic carbon, phosphate and sulphate concentrations of water and sediment were manyfold greater in Khodiyar than Pariyej wetland, which could be due to chemical and organic pollution nature and high amount of sewage and domestic wastewaters received by the Khodiyar wetland. It is

KW	Sulphate(w)	Phosphate (w)	Sulphate (s)	Phosphate (s)	OC (s)	CH_4 emission
Sulphate (w)	0	0	0	0	0	0
Phosphate (w)	-0.254	0	0	0	0	0
Sulphate (s)	0.265	0.823	0.000	0	0	0
phosphate (s)	-0.170	0.574	0.696	0	0	0
Organic carbon(s) -0.830	0.160	-0.429	-0.343	0	0
CH ₄ emission	-0.763	-0.549	-0.018	-0.104	0.909	0

Table 1: Correlation coefficient (r) between methane emission and organic carbon, phosphate and sulphate contents of the water and sediment in the Khodiyar wetland.

KW = Khodiyar wetland, w = water, s = Sediment, OC = Organic carbon

Table 2. Correlation coefficient (r) between methane emission and organic carbon, phosphate and sulphate contents of the water and sediment in the Pariyej wetland.

PR	Sulphate(w)	Phosphate(w)	Sulphate(s)	phosphate(s)	OC(s)	CH ₄ emission
Sulphate (w)	0	0	0	0	0	0
Phosphate (w)	0.423	0	0	0	0	0
Sulphate (s)	-0.358	-0.036	0	0	0	0
phosphate (s)	0.020	0.911	0.042	0	0	0
Organic carbon	(s) -0.793	-0.751	-0.143	-0.439	0	0
CH_4 emission	-0.070	-0.911	-0.300	-0.952	0.589	0

PR = Pariyej wetland, w = water, s = Sediment, OC = Organic carbon

further confirmed that the increased phosphate and sulphate concentrations of water and sediments gradually suppressed the concentration of methane release. Kang & Freeman (2004) also observed similar pattern of methane emission that the rate of methane emission shooted up when the phosphate and sulphate content in both the wetlands were poor.

The correlation coefficient (r) showed that the methane emission has positive correlation with the organic carbon content (0.909 and 0.589 for Khodiyar and Pariyej wetland, respectively), and negative correlation with the phosphate (-0.104 and -0.952 for Khodiyar and Pariyej wetland, respectively) and sulphate (-0.018 and -0.300 for Khodiyar and Pariyej wetland, respectively) content of the sediment in the Khodiyar and Pariyej wetlands. On the other hand, sulphate content of water (-0.763 and -0.070 for Khodiyar and Pariyej, respectively) and phosphate content of water (-0.549 and -0.751 for Khodiyar and Pariyej, respectively) showed negative relation with the methane release (Tables 1, 2).

The results of single factor ANOVA showed that the values of the studied parameters differed significantly for both the wetlands (F_{KW} 9.91; $p < 0.0; \pm = 0.05$) and (F_{PR} 28.26; $p < 0.0; \pm = 0.05$). Similar correlation was established using two-sample variances F-test among studied parameters for the whole experiment ($F_{SO4(s)}$ 35.51; $p < 0.0; \pm = 0.05$), ($F_{PO4(s)}$ 431; $p < 0.0; \pm = 0.05$), $F_{SO4(w)}$ 0.003; $p < 0.0; \pm = 0.05$), ($F_{PO4(s)}$ 1.2; $p < 0.0; \pm = 0.05$) (F_{OC} 21.73; $p < 0.0; \pm = 0.05$) and (F_{CH4} 1337; $p < 0.0; \pm = 0.05$).

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