Estimation of Methane from Kerala - Konkan Onshore Peatlands of South West Coast India by Ground Penetrating Radar Method*

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Abstract

Peatlands are significant in generation of methane can be a clean energy resource in future. Quaternary Peatlands of West coast of India have abundant peat deposits, less studied by researchers. For this study, we used non-invasive Ground Penetrating Radar Method (GPR) to investigate gas dynamics in peatland along with the direct measurement emission rate. This technique has not been used to explore the distribution and release of biogenic gas in Indian Peatlands. Therefore, the present research aims to identify the presence and saturation of biogenic methane in humid tropical peatland of Kerala coastal inlands of South West Coast of India. We have conducted field scale survey with GSSI GPR system, using 100 MHz frequency shielded antennas and direct core sample collection for lab experiments. The presence of shadow zone and variations in EM velocity and amplitude of radar signals were analysed to identify the thickness and geometry of the peat from the common offset radargram. Semblance analysis from the Common Midpoint (CMP) data used to estimate the two-way travel time of reflections from each layer and from the petrophysical model, we have calculated gas percentage at respective depths. The compositional analysis by GC-MS results 92% of methane, 0.5% of CO₂ and 7.5% of N₂ within the collected gas indicates its biogenic nature. Peat/carbonaceous clay act as both source rock as well as reservoir rock. The gas is considered present in the state of free gas in the porous medium (within the peat matrix) and as adsorbed gas onto the surfaces of the peat matrix. Our results show the vertical and spatial variations in biogenic methane content in shallow portions (<22m) of stratigraphic column where the peat has sandwiched between confining clay layers. The results are relevant in the current scenario of unconventional energy resources exploration from a new sedimentary setting

Introduction

Peatlands are formed by the slow accumulation of partially decayed vegetal matter deposited in a basin flooded with water, prevents the flow of oxygen from atmosphere and created anoxic condition, which leads to a low rate of decomposition of organic detritus. These are locations are well known for the generation, accumulation and release of methane. Though South West India has extensive wetland system in which the total estimated wetland (peatland) area of Kerala extends up to 1279.30 Km² comprising 342 Km² of 'inland wetlands' and 937.30 Km² of 'coastal wetlands' (Nair, 2007), stands first in having large area of wetlands in India (Nayar and Nayar, 1997), received less attention except peat swamp

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of (a) Late Pleistocene from the Nilgiri Hills, a mountain region more than 2,000 m a.s.l. in southern India (Rajagopalan et al., 1997) and that of (b) Himalayan Basin (Phadtare and Pant, 2006). Both these studies were limited to exploring the paleoclimate potential of this unique sedimentary record. The main goal of our study is to estimate the spatial and vertical variations in of biogenic gas saturation and dynamics in SW coast of India, especially Alappuzha region, which is selected as the most potential site established from Ground Penetrating Radar (GPR) studies and supported by direct gas flux measurement.

Study Area

The geological areas under study are located 1 to 3km away from present day coastline in Alappuzha, Kerala (9 30.46655'N-76 19.58442'E and 9°13.624'N-76°32.533'E) (Figure 1) and are positioned in the quaternary sediment of onshore basin of West Coast of India formed by dynamic shoreline changes and neotectonic activity experienced millions of years Before Present (BP) to recent past. The nearly straight coastline of Kerala trending NNW-SSE undergoes number of transgression and regression phases, which are evidenced from the distribution of fluvio-marine sediments that have been explored from 3 to 4 km east of present day coast. The organic rich deposits of west coast of India have derived mainly from mangrove swamps and form stratigraphic markers of Late quaternary sequence related to the Global sea level rose resulting the formation of three generations of peat – the older, 43,000 - 40,000 ¹⁴C year B.P., Middle Holocene to Late Pleistocene (10,760–4540 ¹⁴C year B.P.) and the Late Holocene <4000 ¹⁴C year B.P. (Narayana et al., 2001a). Carbonized wood/ peat deposits and organic rich sediments related to mangrove are widely reported in different parts of west coast of India in the above periods (Jayalakshmi et al., 2004).

Methodology

Ground Penetrating Radar

Two types of operational mode have been adopted for the present study, in which the most common operation mode is the constant-offset profiling by 100 MHz antenna. In this method, the transmitter and receiver are separated by a fixed distance. The two-way travel time of the EM wave from the surface transmitter to reflectors at depth and returned to the surface receiver is recorded. The survey has been used to image the stratigraphy, peat depth and the locations of possible confining layers. The scattering of EM energy ("EM blanking") by free - phase gas (by the displacement of water by hydrocarbon gas vapours) results in regions of faint or absent reflectors in radargram (Daniels et al., 1995). Lopes de Castro and Branco (2003) identified regions of strongly attenuated reflections or shadow zones due to the build-up of hydrocarbon vapours while monitoring hydrocarbon leakage by GPR. Another operational mode is Common Midpoint (CMP) Survey, where two-way travel time is recorded by 100MHz antenna in bistatic mode by manually moving the transmitter and receiver apart from a centre point stepwise while collecting data. This was used to determine 1-D vertical velocity structure. GPR data were processed by 'de-wowing', (removal of low frequency components) and linear/exponential gain function to amplify late time return signals. Time zero correction of each trace before the first arrival was omitted to correct the start time. Migration was used to correct the slope of dipping reflectors, reduce the effect of point diffractions (Neal, 2004), and place the events back in the correct spatial locations by collapsing local diffraction hyperbolae.

Stratigraphy of peatland using common offset GPR

GPR is a geophysical technique well suited for investigating subsurface stratigraphy in low electrical conductivity environments (Davis and Annan, 1989; Neal, 2004). A transmitting antenna generates a continuous high-frequency electromagnetic (EM) wave that penetrates the subsurface and is returned as a sequence of reflections from stratigraphic interfaces due to changes in the electrical properties (primarily dielectric permittivity) of the subsurface. The common offset radargrams were used to reconstruct the 2-D stratigraphic image of the study site (Figure 3). The GPR data require signal enhancement preceding interpretation due to attenuation by the presence of ionic molecules and several noise sources during data acquisition. The data processing steps include removal of D.C. offset, waveform-to-waveform shifts, band pass filtering and removal of the coherent background noise. The gain function is the resultant of the average amplitude of all the wavelets and it is applied to each wavelet. Gain is applied to overcome attenuation, which is generated due to dielectric loss by conductive medium, geometrical spreading and antenna coupling. Despite the gain function being applied, the relative amplitude between traces was retained. Migration technique was applied to the data to enhance the resolution of unambiguous features.

Estimation of Free Phase Gas (FPG) Content using Common Midpoint (CMP) GPR

The spatial variability of FPG volume was investigated non-invasively across multiple peatland locations by determining EM velocity (Comas et al., 2007). The velocity of electromagnetic waves (EM) through a medium is determined by CMP method. In this method, transmitter and receiver are continuously separated by a known interval following each pulse of EM radiation. The two-way travel time increases with increase in distance between transmitter and receiver are used to determine velocity. The volumetric content of the sedimentary environments was studied using CMP method by Huisman et al., 2003. The EM velocity is related to the bulk dielectric permittivity ($\epsilon_{r(b)}$) of the subsurface medium,

$$v = \sqrt{\frac{c}{\varepsilon_{r(b)}}}$$
 (1)

where v is EM velocity and c is the speed of light in vacuum. Electromagnetic wave velocity was determined from the CMPs by fitting a reflection hyperbola to the mineral soil reflector

$$t_x^2 = \frac{x^2}{v^2} + t_0^2 \tag{2}$$

where t_x is the two-way travel time at x distance separation between antenna, v is EM wave velocity and t_0 is the zero- offset travel time. When t_x^2 is plotted against x, a linear relationship can be fitted to the data with a slope of 1/v and intercept of t_0^2 . 1-D velocity profile was determined by fitting reflection hyperbola in continuous reflectors within the peat column, which was selected, with the help of semblance analysis (Huisman et al., 2003, Parsekian et al., 2010). Semblance analysis shows arrival times for the reflected waves and recalculates arrival

times for a series of velocities resulting in a semblance plot (arrival time vs. velocity). Reflectors with high semblance are picked up manually in the plot and the interval velocities of individual reflectors are calculated using Dix formula (Huisman et al., 2003)

$$v_{int,n} = \sqrt{\frac{t_n v_n^2 - t_{n-1} v_{n-1}^2}{t_n - t_{n-1}}}$$
(3)

where $v_{int,n}$ is the average velocity within the interval with reflector n at its base and n-1 at its top surface, t are the two-way travel times from the peat surface to the bottom layers n and n-1, and v_n and v is the average velocity from the surface to the bottom of layers n and n-1. The Complex Refractive Index Model (CRIM), a mixing model for soil, was used to estimate gas contents from EM wave velocities according to the equation given by Huisman et al. (2003):

$$\varepsilon_{r(b)}^{\alpha} = \theta \varepsilon_{r(w)}^{\alpha} + (1-n)\varepsilon_{r(s)}^{\alpha} + (n-\theta)\varepsilon_{r(a)}^{\alpha}$$
 (4)

where $\varepsilon_{r(\alpha)}$, $\varepsilon_{r(w)}$ and $\varepsilon_{r(x)}$ are the relative dielectric permittivity of gas (equals 1), water and soil particles respectively; θ is the volumetric water content; n represents porosity and α accounts for the orientation of the electromagnetic field to the subsurface particle arrangement and has been assumed as 0.35 for peat. Assuming the value of α has determined the judicious estimates of gas content (Kellner and Lundin, 2001; Keller et al., 2004; Comas et al., 2008).

Direct Field measurements

Gas flow rate estimated from three sites estimated by inserting PVC pipe of 2-inch diameter up to a depth of 17m, 19m and 22m where the flow encountered while drilling. Gas flow regulated by valve above the ground with PVC pipe of 1-inch diameter and it connected with a flexible pipe to the bucket filled with saltwater solution (Figure 2). The Winchester bottle fully filled with salt water kept upside down inside the bucket and end of the pipe inserted into that. The gas flow regulated by valve and measured at 3 hours interval. The rate of emission of gas is measured by the displacement method according to Henry's law.

Gas chromatography (GC-MS)

Free phase gas samples were directly collected from the potential sites (Figure 1) by inserting pipe to the ground at designated depths (17-22m) obtained from GPR results can controlled by valve fitted on the ground. Samples were collected using glass bottle method by Winchester bottle of 1-liter capacity. A schematic representation of gas sample collecting mechanism has shown in Figure 3. Gas samples were transported to the laboratory for the analysis with a Varian 3600 GC/ FID/TCD gas chromatograph. Gas chromatography is used to separate the components of the mixture, identify the components based on their retention time and determine the percentage of composition of the mixture from peak areas of unknown gas and can determine physical parameters of gas samples.

The gas samples were analyzed for the relative concentrations of hydrocarbons (C_1 - C_6), CO_2 , and air, using an HP 5890 Series II Gas Chromatograph (GC). The presence of H_2S gas was detected by olfactory means. The GC uses two methods of detection: a flame ionization detector (FID) and a thermal conductivity detector (TCD). The FID determines the concentrations of the combustible hydrocarbons, is very selective, and has a large linear range. The TCD detects the change in thermal conductivity by comparing the thermal conductivity of the carrier gas (helium) with that of the He diluted gas sample. The TCD has a much lower sensitivity than the FID, but is necessary to obtain the concentration levels of the non-combustible CO_2 and air. Each sample was injected into a 95.2 μ L loop, and the ambient temperature and pressure were recorded. The samples were then reanalyzed using a 1.002mL sample loop to increase the detection limit for gases present in very low concentration. A standard gas mixture was also analyzed at both the beginning and end of the sample set for calibration. The data were integrated using HP ChemStation software.

To determine the concentrations of the gases in each sample, peak area analysis was used in combination with response factors calculated from the standard gas mix. The calculations for the response factors and concentrations are as follows:

$$R = \frac{A_{std}}{C_{std} \times 10^4} = \left(\frac{Area}{ppm}\right)_{(5)}$$

$$C = \frac{A_{smp}}{R \times 10^4} = (\%) \tag{6}$$

Where R is the response factor, A_{std} is the peak area of the gas in the standard at STP, C_{std} is the concentration of gas in the standard (%), A_{smp} is the peak area of the gas in the sample at STP, and C is the concentration of gas in the sample as a percent of the total.

Results

The common offset surveys are used for subsurface imaging purposes (since profiles resemble a geological cross-section where depth is expressed as a travel time of the EM wave). Four radar facies and two types of radar surfaces were identified (Figure 3) with a significant dominance of good continuity. Geometry reflectors ranging from subparallel to curved concordant termination appear restricted to the surface of the profile. This was interpreted as radar facies 1 (F1) trapping aeolian sand on the beach ridges. Radar facies 2 (F2) was represented by thick strata with high amplitude reflections which was interpreted as organic rich zone (peat) correlated with the borehole data (Kumaran et al., 2005). The virtual transformation of the forests into peat and buried palaeo forests that remain submerged within the lowlands indicates that peat formation and uniform peatland development took place in a narrow time frame when the rising sea levels stabilized and fell slightly during the Middle Holocene (6.5–5.0 k yrs BP). A combination of factors like the low topographic relief, impermeable substrates and high rainfall has provided favourable conditions for accumulation of organic material and subsequent conversion of organic material into thick deposits of peat. Radar facies (F3) signified transgressive lagoonal spit and marine or nearshore lagoonal environment of deposition. Both these have access to land drainages contribute sediments of different geologic or physiographic settings. The marine/nearshore lagoonal environment of deposition occurred within the depth of 9-11m. The truncational terminations with moderate amplitude indicated nearshore/littoral environment of deposition at the depth of 12m which is denoted as radar facies 4 (F4). The reflection scattering or loss of reflections was

noticed at the depth of 4-8m. The overlying high amplitude reflections with average thickness of 3m can be assumed as the biogenic gas layer with a high velocity. The location of the woody area is characterized by the presence of hyperbolic diffractions in the GPR record (Figure 3) (Comas et al., 2015). EM wave shadow zones (scattering of EM signal) recorded with surface Common offset GPR surveys correlate with areas of biogenic gas accumulation (Figure 3). The Presence of strong reflectors above shadow zones may represent confining layers of clay act as gas traps.

The interpreted reflectors from CMP data has mapped at 3 m, 5 m, and 7 m depths fit with three low velocities (indicative of low gas content) and with maximum velocities (indicative of high gas content) (Figure 4). Figure 3 denotes general view of over pressurized biogenic gas pockets overlain by confining layers acting as biogenic gas traps (Romanowicz et al., 1995; Glaser et al., 2004). Peat/woody fragments and clay rich horizons act as the confined layers. The observed bubble release during borehole installation may be due to the result of disturbance of these confined layers.

The gas content is calculated from the CRIM 1-D vertical velocity model showing the gas content ranges from 0-40%. Gas chromatography analysis results the composition of C1-92% and CO2-0.5% and N2-7.5 by one injection of gas samples. The result accentuates the free phase gas being mainly derived biogenic ally through bacterial methanogenesis from peat deposits, without mixing with thermogenic-originated gas. Gas chromatography is used to separate the components of the mixture, identify the components based on their retention time and determine the percentage of composition of the mixture from peak areas of unknown gas (Figure 5) and determine physical parameters of gas samples (Table 1). With regard to the chemical composition of all the samples analyzed, methane was found to be dominant with 92% occupancy, along with small amounts of CO_2 (0.5%) and N_2 (7.5%) (Figure 5, Table 1). The samples depleted in C_2 ⁺, are assigned as microbial gas generated in the sediment of the early diagenesis stage, though the possibility of thermogenic gas cannot be totally excluded because the C_2 ⁺ hydrocarbons tend to dissipate during long distance migration (Jung-Nan Oung et al., 2006) (Figure 6). Almost all the biogenic gases in reservoirs are characterized by the C isotope of a CO_2 reduction pathway (Schoell et al., 1988; Rice et al., 1992; Noble et al., 1998).

Conclusions

The spatial variations of EM wave shadow zones coincides with areas of biogenic gas accumulation at the depth of 5m and 17-22m at two study areas of Alappuzha peatlands of SW India. The presence of strong reflectors above shadow zones may represents confining layers with carbonaceous rich clay act as gas traps. The subsurface saturation of biogenic gas is 0-40% with dominating methane of 92%. An abrupt changes in gas flux observed is 3-12m³/day, in which the flow is intermittent to continuous within 3 km² area. These findings also have implications for the monitoring of spatial and temporal behaviour and variability of biogenic gas emissions from Southwest Indian peatlands.

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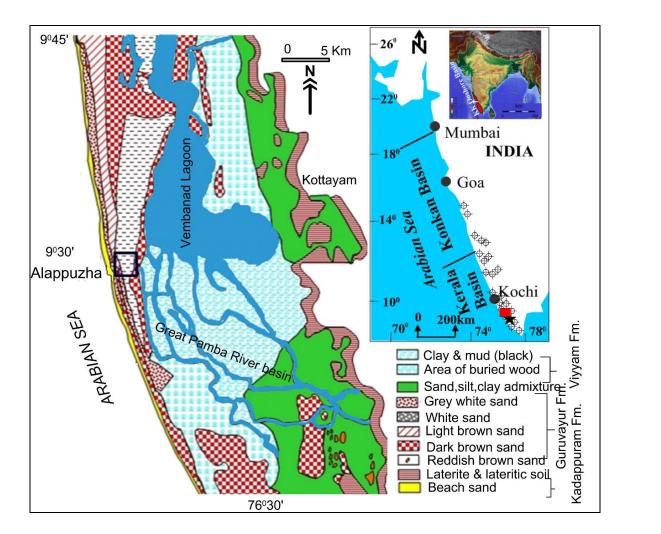


Figure 1. The study area in Alappuzha, where extensive study done and inset map showing the GPR data acquired locations along SW coast of India (modified from K. K. Nair, 2007).

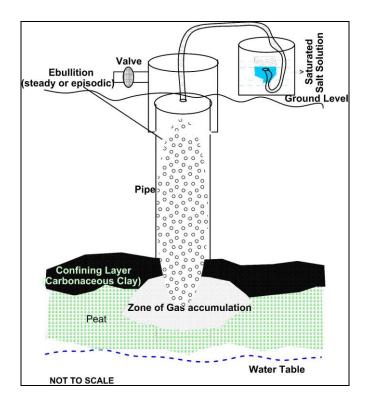


Figure 2. Schematic diagram of gas sample collection.

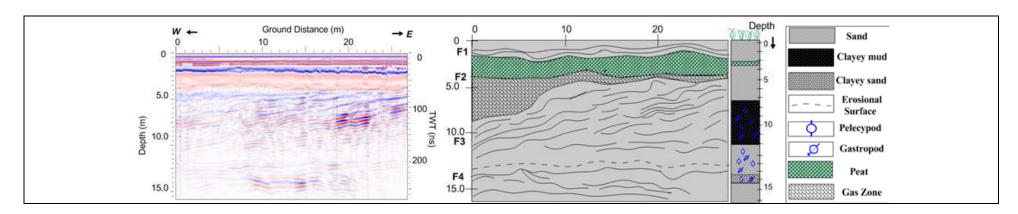
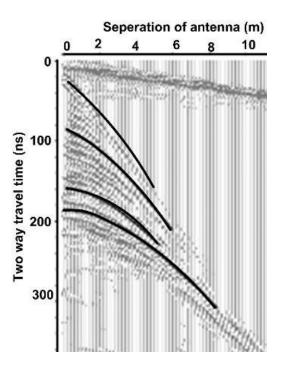


Figure 3. Surface constant offset GPR profiles collected from Alappuzha using 100MHz monostatic antenna, bore hole data modified from K.P.N Kumaran et al., (2005).



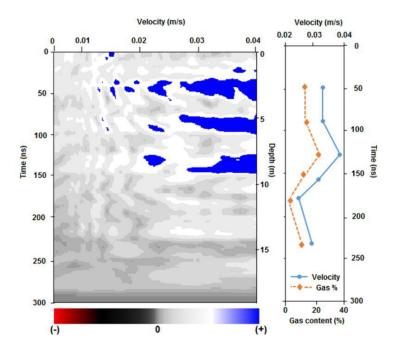


Figure 4. Vertical distribution of FPG derived from CMP semblance analysis and gas percentage calculated using CRIM model (from Alappuzha few km away from the common offset location).

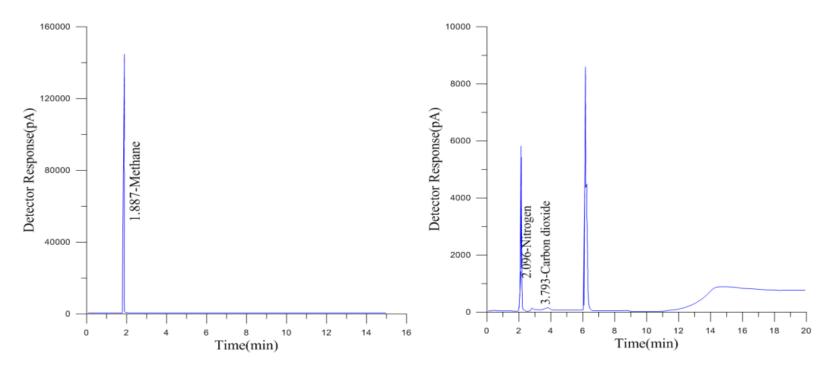


Figure 5. Example of Gas chromatograms of gas collected from Alappuzha (9° 30. 500' N, 76° 19. 868'E) with significant amount of C1+ in chemical composition, inferring its biogenic (microbial) origin. (a) FID1A, front signal (b) TCD2B, back signal; with retention time in x-axis and detector response in y-axis.

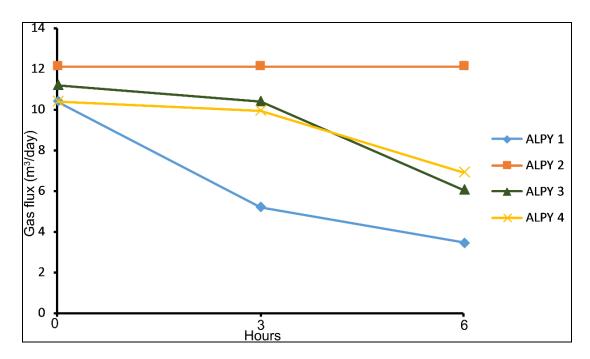


Figure 6. Direct gas flux measurements from most prospective areas.

	Components											Parameters		
	C ₁	C ₂	C ₃	iC ₄	nC ₄	iC ₅	nC ₅	C ₆₊	CO ₂	N ₂	Не	Calorific value (net) on real gas basis at 15.6°C and 14.73 psia (Kcal/m³)	Specific gravity	Compressibiliy factor (Z)
Sample 1 (17m) (ALP1)	92.01	0	0	0	0	0	0	0	0.50	7.49	0	7474.17	0.59123	0.998168
Sample 2 (22m) (ALP 4)	92.14	0	0	0	0	0	0	0	0.48	7.38	0	7484.75	0.59123	0.998166

Table 1. Gas chromatography analysis of samples collected from the study site with the physical parameters collected correspondingly obtained from gas chromatograph. The spatial and temporal variations of methane flux from the deeper peat layers (17-22m) varies from 3.4 to 12.09m³/day. The emission varies from continuous to fluctuating in each location.