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Research Article

Shallow Surface Geochemical Assessment of Subsoil Methane Deposits and its Implications

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Keywords

Biogenic methane, Gas chromatography-mass spectrometry (GC-MS), Isotope, SW Indian peatlands.

Abstract

Organic rich soils (peat) store significant amounts of global soil carbon in the form of methane (CH_4) and carbon dioxide (CO_2). Understanding both physical and biological processes of natural gas generation in peat is essential to find a better insight into the origin of shallow natural gas reservoirs in the South-West coast of Indian peatlands. This work discloses the composition and source of hydrocarbon escaping through the boreholes or weaker zones from shallow peat overlain by carbonaceous clay by using the methods of GC-MS and stable isotope analysis ($\delta^{13}C_{CH4}$ and δD_{CH4}). The natural gas compositions are characterized in this study by considering a three-component mixture of 92 mol% CH_4, 0.5 mol% N_2 and 7.4 mol% CO_2 with varying temperature ranges and pressure of 101.3KPa. Our research hypothesis highlights the emanating natural gas being mainly derived through bacterial methanogenesis from organic matter rich peat by CO_2 reduction pathway without mixing with thermogenic or landfill gases.

1. Introduction

Peat are the organic matter (OM) rich deposits formed during the process of plant to coal transition mostly generates methane and stores within voids under favorable conditions. These trapped gases also known as biogenic gas generally developed in immature regimes from bacterial mediated anaerobic mineralization of organic matter in sediments [1]. Globally biogenic gas accumulations may account for 30% or more from natural resources and may dominate in individual biogenic reservoirs [2]. The methane formation and accumulation happen through multiple pathways includes carbonate reduction and fermentation and also formed either from shallow sedimentary organic deposits or from pre-existing oil accumulation or from both the sources. The produced in-toxic methane is relatively insoluble in water and removed rapidly via ebullition as bubbles [3], in the case of absence of confining stratum and these trapped gases are utilized for this study.

Gas Chromatography (GC) technique is widely used in geochemical studies [4]. One of its extensive applications is the determination of gaseous hydrocarbons (C_1-C_5) and non-hydrocarbons gases (N_2, CO_2, H_2, O_2) in marine sediments. The knowledge of composition and concentration of these gaseous is used to constrain the origin of gases [5], along with the stable isotope analysis of C and H in the CH_4. In addition to the source studies, the moisture analysis of the generated natural gas is significant for sustaining a stable and safe processing and transport. The underestimate of moisture in natural gas lead to the condensation of liquid water in process equipment and pipelines; and other consequence is the formation of gas hydrates [6].

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The importance of identifying the composition of natural gas has many implications, such as to assess the origin of methane, to understand the environment of formation and natural gas resource. The process of methanogenesis is the final step in biodegradation of OM, producing CH_4 and CO_2. The methanogenic pathways are directly related to the history of OM deposition and the upstream biogeochemical processes that generate substrates required by methanogens. Hence, it is important to identify the different environments of methanogenic pathways to understand OM decomposition and greenhouse gases fluxes [7]. The active methanogenesis process in a system can stimulate and can yield more gas resources by the understanding of methane generation mechanisms [8]. The near surface formations (for example, shales and coal bed methane) containing biogenic gas gone through hydraulic fracturing [9], so the finding of biogenic gas is of major interest. In this scenario, the unconventional natural gas in the peatland and its extraction grows in economic importance.

2. Study Area and Geological Settings

The study sites are located in ~2km far from present day coastline in Alappuzha, SW coast of India (Figure 1), is positioned in the Holocene-Pleistocene sediments formed by dynamic shoreline changes and neotectonics activity experienced in millions of years BP to recent past. The nearly straight coastline of Kerala trending NNW-SSE undergoes number of transgression and regression phases evidenced from the distribution of fluvio-marine sediments have been explored from few kilometers inland 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 results 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. [10].

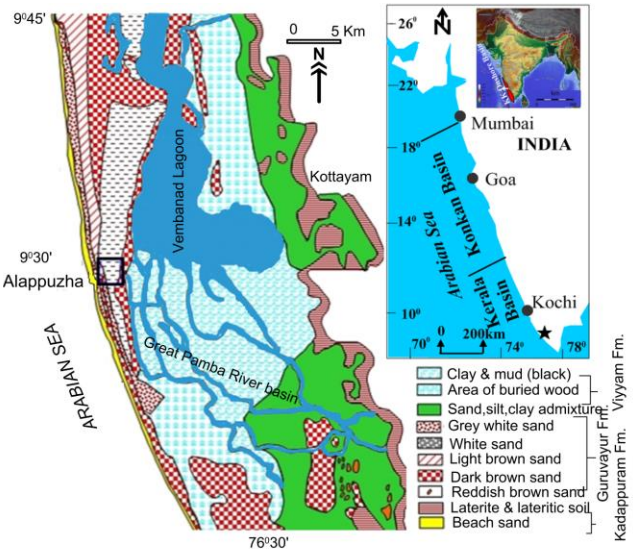

Figure 1. Location map of West coast India showing the study site, Alappuzha comes under Kerala onshore basin of KK basin (modified from [11])

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 [12]. The study area falls under Viyyam formation (Figure 1 and Table 1), the litho-units of Viyyam surface, comprises of fluvio-marine deposits and the formation consists of the deposits of tidal flats, mud flat, estuarine landforms, and delta. The distinct lithology in this formation consists of a top layer of black/grey black, sticky, plastic clay with pockets of fine sand (~50 cm thick), followed by a middle layer of black clay with shells and buried wood (~1m thick) and lastly a black organic clay layer of >1m thick. The low land area of Alappuzha occurred with thick pile of buried wood at shallow depth is reminiscent of subsidence of the terrain and burial of luxuriant mangrove forest that existed along coastal area. The rapid and complete carbonization of this buried wood undergoes with lower sandy stratum and upper clay layer with overburden pressure. The resultant carbonized wood has been found in highly decomposed state and preserved in sheath of sediments. During this process of carbonization methane evolved and getting trapped by overlain clay.

3. Methods

After rotary drilling, a PVC pipe was inserted in boreholes of ~20m depth. Natural gas in free state that emitted from the boreholes was collected in a glass vessel (Winchester bottle) of 1000 ml capacity saturated with NaCl solution, which was flushed, and half filled with “free” gas under pressure (Figure 2). The sampled gas stored under normal atmospheric condition had to be analyzed for chemical composition and isotope analysis of carbon and deuterium in methane. The gas samples were transported to the Regional Geoscience Laboratory, ONGC, Chennai, and analyzed using the Varian 3600 GC/FID/TCD gas chromatograph. The method for assessing $\delta^{13}C_{CH4}$ and δD_{CH4} using gas chromatography-isotope ratio mass spectrometry is described in [13]. The humidity and other physical properties of the ebullitive gas were measured from the field by using an Insitu-thermo hygrometer and plotted in a psychrometric chart.

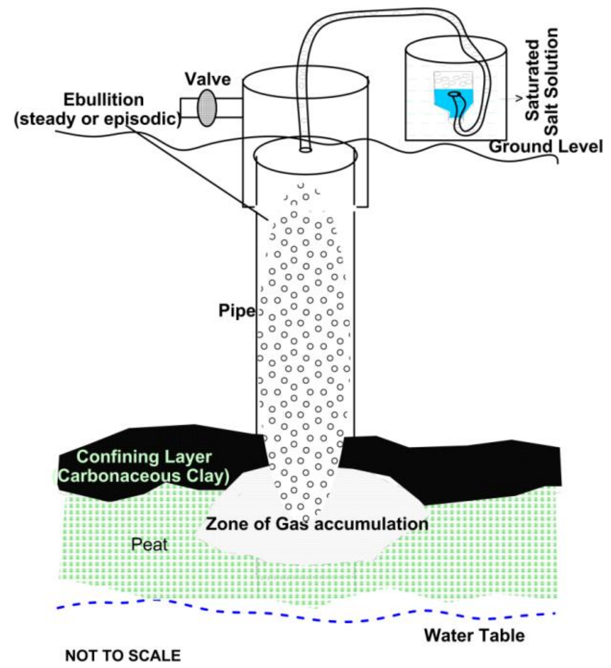

Figure 2. Schematic diagram of gas sample collection from field

Table 1. Quaternary Geological succession of Alappuzha region

Period	Age	Environment	Geomorphic Unit	Landform	Morpho stratigraphic Unit	Lithology
Quaternary	Late Holocene	Marine	Kadappuram Surface	Beach, Barrier beach	Kadappuram Formation	Sand, coarse to fine sand
	Mid- Holocene	Fluvio Marine	Viyyam Surface	Tidal flat	Viyyam Formation	Clay and silt black and greyish black in color with wood fragments
	Early Holocene	Fluvial	Periyar Surface	Flood plain	Periyar Formation	Sand, silt, clay admixtures
	Early Holocene to Late Pleistocene	Marine	Guruvayur Surface	Strand plain with trend line	Guruvayur Formation	Mostly sand with little amounts of clay and silt
Upper Tertiary	Pliocene	Erosional	Kunnamkulam Formation	Upland	Kunnamkulam Formation	Primary laterite

4. Results and Discussion

4.1. Compositional Analysis of Natural Gas

GC-MS method was utilized for this study to separate components of the natural gas mixture and identified the components based on their retention time to determine the percentage of composition of the mixture from peak areas of unknown gas and physical parameters of gas samples (Table 2). With regard to the chemical composition of the two samples analyzed, methane was found to be dominant with 92% occupancy, along with minor amounts of CO_2 (0.5%) and N_2 (7.5%) without mixing with H_2S (Table 2).

Table 2. Gas chromatography analysis based on value % mole in moisture free basis of gas samples, isotope analysis results and physical parameters pertaining to gas samples correspondingly obtained from gas chromatograph.

Gas Components and Parameters	S1	S2
C_1	92.01	92.14
C_2 - C_{6+}	0	0
CO_2	0.5	0.48
N_2	7.49	7.49
$\delta^{13}C_{CH4}$ (‰)	65	68
δD_{CH4} (‰)	214	202
Calorific value (net) on real gas basis at 15.60C and 14.73 psia (Kcal/m^3)	7474.17	7484.75
Specific gravity	0.59123	0.59058

The samples are depleted in C_2^+, are assigned as microbial gas generated in the sediment of the early diagenesis stage. In addition to the compositional analysis, stable isotope analysis of C and H in the CH_4 was carried out to confirm the source of origin of the ejecting natural gas. The rate of production and accumulation of biogenic gas in a basin depends on how fast sediments are buried and reach a temperature above which microbial activity stops and this sediment is exposed to a stratum and microbial activity continues. The factors controlling the thermal activity are the nutrient supply and microbes present in the subsurface. The activity of microbes starts to reduce at about 500C [14] and ends at or beyond 800C.

4.2. Source of Origin of Natural Gas

A dual plot of carbon ($^{13}C/^{12}C$) and hydrogen ($^{2}H/^{1}H$) isotope ratios of CH_4 are useful to distinguish microbial and thermogenic CH_4 from the organic-rich sedimentary environment (Table 2 and Figure 3) [15], also to identify pathways of production of biogenic methane [16]. Through this analysis, we were able to distinguish the methane generated from landfills, coal bed gas, natural gas, and glacial drift gas. The ratios of hydrogen and carbon isotopes relative to the isotopic composition of VPDB (Vienna Pee Dee Belemnite) and VSMOW (Vienna Standard Mean Ocean Water) expressed in δ, in units per mille (‰). The current isotope analysis of methane results, the carbon isotope values ($\delta^{13}C_{CH4}$) range between −65‰ and −70‰, and hydrogen isotope values (δD_{CH4}) range from −188‰ to −220‰, which indicate that these natural gases are biogenic in origin and formed by the CO_2 reduction pathway.

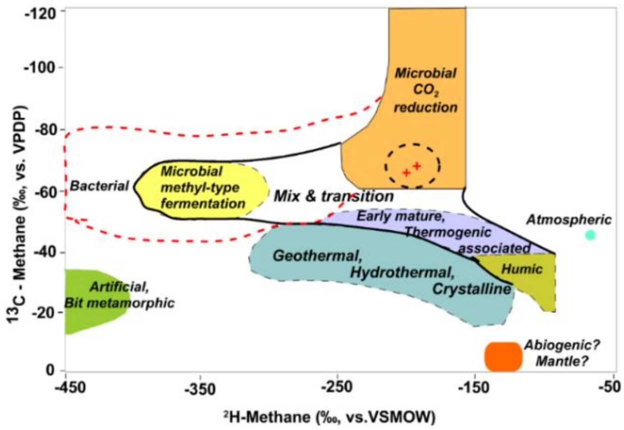

Figure 3. C and H signatures of CH_4 sources represented by CD diagram (modified from [17]). The figure shows the classification of bacterial and thermogenic natural gas by combination of $\delta^{13}C_{CH4}$ and δD_{CH4} information. The samples fall in the microbial CO_2 reduction pathway.

Globally, researchers have developed geochemical and isotopic indicators for identifying biogenic methane of rocks in methanogenic sedimentary basins [18]. The origin and distribution of methane sources have been discussed previously [19]. The produced methane is trapped in shallow and immature environments like sub-littoral marine bays, marine sediments, anoxic fresh water likes, swamps, glacial drifts, and paddy fields below the anaerobic sulphate-reducing zone [20]. The deltaic areas that are rich in clay deposits with a continuous supply of OM produce biogenic methane [21].

4.3. Physical Properties of Natural Gas and its Implications

Moisture or absolute humidity of the natural gas has been analyzed using an in situ thermo hygrometer by measuring temperature as well as relative humidity (RH) and other properties from the psychrometric chart (Table 3 and Figure 4). These physical properties are significant in upstream processes such as design and operations of processing systems, transportation, and storage of natural gas due the condensation behavior of water vapor. The physical properties of natural gas are represented graphically in the psychrometric chart (Figure 4).

Table 3. Results from psychrometric chart.

Sample Points	DB (^{0}F)	WB (^{0}F)	RH (%) from Psychrometric Chart	RH (%) from Insitu Thermo Hygrometer	SD in RH	W (gr/lb)	V (ft^3/lb)	Vp (inches Hg)	d (lb/ft^3)	Aw (gr/ft^3)	h (Btu/lb)	DP (^{0}F)
S1a	87.8	80.6	73.57	74.2	0.445	147.57	14.28	0.98	0.07	10.34	44.28	78.3

S1b	87.9	80.9	74.27	73.8	0.332	149.53	14.29	0.99	0.07	10.47	44.61	78.69
S1c	91	81.6	67.31	70.9	2.538	149.38	14.37	0.99	0.07	10.4	45.36	78.66
S1d	90.8	80.9	65.68	68.9	2.277	144.71	14.35	0.96	0.07	10.09	44.58	77.73
S2a	87	81.6	79.63	73.3	4.476	156.03	14.28	1.03	0.07	10.92	45.41	79.94
S2b	86.5	79.5	73.91	70.9	2.128	142.09	14.23	0.94	0.07	9.99	43.09	77.19
S2c	91.7	83.4	70.99	68.8	1.549	161.46	14.42	1.07	0.07	11.19	47.44	80.95
S2d	93.5	83.6	66.53	68.2	1.181	159.97	14.47	1.06	0.07	11.06	47.66	80.67

The graph represents physical properties as a function of changing parameters (RH, wet bulb, and dry bulb temperatures) of non-condensing components and a single condensing vapor component of the natural gas. The natural gas compositions are characterized in this study by considering a three-component mixture of 92 mol% CH_4, 0.5 mol% N_2 and 7.4 mol% CO_2 (from GC-MS) with varying temperature ranges (from the in situ-thermo hygrometer) and pressure of 101.3KPa.

The heating value of natural gas decreases with high water content and it can also trigger the formation of gas hydrates within the pipelines, causing blockage and corrosion. The corrosion occurs due to the formation of acids caused by the reaction of water vapor with natural gas trace contaminants like H_2S and CO_2. Due to all these reasons, measurement of humidity is essential. The psychrometric chart was limited to the humid air system of water vapor in dry air, but recently its application has extended to water vapor in natural gas [22].

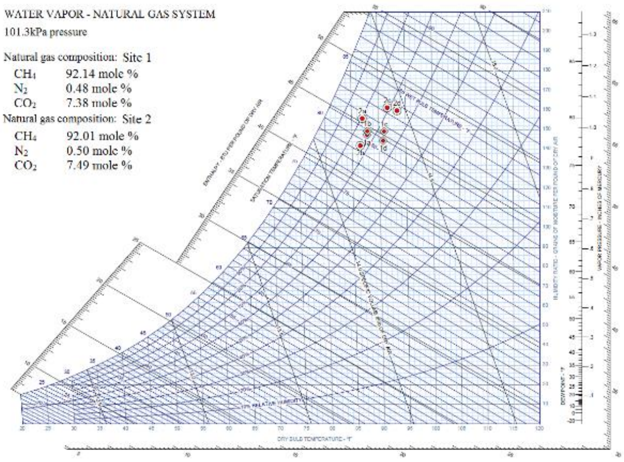

Figure 4. Psychrometric graph plotted based on the compositional analysis, temperatures, and RH from emanating sample (S1 and S2) boreholes for determining the physical parameters of the gas samples.

5. Conclusion

The primary biogenic gases are concentrated in Quaternary (Holocene) successions characterized by rapid sedimentation, high organic matter content (woody fragments and peat) and syn-depositional entrapment of carbonaceous clay. The geochemical composition (CH_4, CO_2, N_2) and isotopic tracers ($\delta^{13}C_{CH4}$ and δD_{CH4}) furnished the geochemical and isotopic characterization of "peat" gases from SW Indian Peatlands. The deuterium of methane (δD_{CH4}) has been used to identify the origin of methane by comparing worldwide sedimentary basins methane. The results shows that the "peat" gas is dominated by methane (92%) without any H_2S, and the $\delta^{13}C_{CH4}$ - δD_{CH4} analysis provides evidence of the microbial origin of the natural gas through the process of CO_2 reduction. The current investigation in shallow biogenic methane emissions from the peat is relevant not only because of safety and environmental concerns but also due to the resource potential of methane. Demand for energy is high in the thickly populated area and the risk of an environmental hazard due to the migration and escape of these gases to the surface through the weaker zone have to be considered. If the existing methane could be collected instead of being left to reach the atmosphere through diffusion and ebullition as GHG, these shallow biogenic gas systems could provide an important energy resource to meet the demand for natural gas.

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Conflict of Interest Statement

The authors declare no conflict of interest.

References

[1] D.D. Rice, G.E. Claypool, Generation, accumulation, and resource potential of biogenic gas, AAPG bulletin 65 (1981) 5–25.

[2] B.J. Katz, Microbial processes and natural gas accumulations, The Open Geology Journal 5 (2011).

[3] C.S. Martens, J.V. Klump, Biogeochemical cycling in an organic-rich coastal marine basin—I. Methane sediment-water exchange processes, Geochimica et Cosmochimica Acta 44 (1980) 471–490.

[4] E. Galimov, L. Kodina, O. Stepanets, G. Korobeinik, Biogeochemistry of the Russian Arctic. Kara Sea: Research results under the SIRRO project, 1995–2003, Geochemistry International 44 (2006) 1053–1104.

[5] N. Safronova, E. Grishantseva, G. Korobeinik, Hydrocarbon gases (C1–C5) and organic matter in bottom sediments of the Ivankovo Reservoir on the Volga River, Water Resources 40(3) (2013) 285-296.

[6] A. Jamieson, H. Sikkenga, On-line water dewpoint measurement in natural gas, Gas Quality, Elsevier Science Publishers BV Groningen (1986) 289–299.

[7] M. Formolo, The microbial production of methane and other volatile hydrocarbons, Handbook of Hydrocarbon and lipid Microbiology 2010.

[8] D. Ritter, D. Vinson, E. Barnhart, D.M. Akob, M.W. Fields, A.B. Cunningham, W. Orem, J.C. McIntosh, Enhanced microbial coalbed methane generation: a review of research, commercial activity, and remaining challenges, International Journal of Coal Geology 146 (2015) 28–41.

[9] R.B. Jackson, E.R. Lowry, A. Pickle, M. Kang, D. DiGiulio, K. Zhao, The depths of hydraulic fracturing and accompanying

water use across the United States, Environmental science & technology 49 (2015) 8969–8976.

[10] K. Kumaran, K. Nair, M. Shindikar, R.B. Limaye, D. Padmalal, Stratigraphical and palynological appraisal of the Late Quaternary mangrove deposits of the west coast of India, Quaternary Research 64 (2005) 418–431.

[11] K. Nair, D. Padmalal, K. Kumaran, R. Sreeja, R.B. Limaye, R. Srinivas, Late quaternary evolution of Ashtamudi–Sasthamkotta lake systems of Kerala, south west India, Journal of Asian Earth Sciences 37 (2010) 361–372.

[12] K. Jayalakshmi, K. Nair, H. Kumai, M. Santosh, Late pleistocene-holocene paleoclimatic history of the Southern Kerala Basin, Southwest India, Gondwana Research 7 (2004) 585–594.

[13] J. Lazar, T. Kanduč, S. Jamnikar, F. Grassa, S. Zavšek, Distribution, composition and origin of coalbed gases in excavation fields from the Preloge and Pesje mining areas, Velenje Basin, Slovenia, International journal of coal geology 131 (2014) 363–377.

[14] J. Clayton, Geochemistry of coalbed gas–A review, International Journal of Coal Geology 35 (1998) 159–173.

[15] D. Strąpoć, M. Mastalerz, K. Dawson, J. Macalady, A.V. Callaghan, B. Wawrik, C. Turich, M. Ashby, Biogeochemistry of microbial coal-bed methane, Annual Review of Earth and Planetary Sciences 39 (2011) 617–656.

[16] R.A. Burke, C.S. Martens, W.M. Sackett, Seasonal variations of D/H and 13C/12C ratios of microbial methane in surface sediments, Nature 332 (1988) 829–831.

[17] M.J. Whiticar, Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane, Chemical Geology 161 (1999) 291–314.

[18] S.D. Golding, C.J. Boreham, J.S. Esterle, Stable isotope geochemistry of coal bed and shale gas and related production waters: A review, International Journal of Coal Geology 120 (2013) 24–40.

[19] M. Schoell, Multiple origins of methane in the Earth, Chemical geology 71 (1988) 1–10.

[20] M.J. Whiticar, E. Faber, M. Schoell, Biogenic methane formation in marine and freshwater environments: CO2 reduction vs. acetate fermentation—isotope evidence, Geochimica et Cosmochimica Acta 50(5) (1986) 693–709.

[21] M. Misuraca, F. Budillon, R. Tonielli, G. Di Martino, S. Innangi, L. Ferraro, Coastal Evolution, Hydrothermal Migration Pathways and Soft Deformation along the Campania Continental Shelf (Southern Tyrrhenian Sea): Insights from High-Resolution Seismic Profiles, Geosciences 8(4) (2018) 121.

[22] D. Shallcross, S. Low, Construction of psychrometric charts for systems other than water-vapor in air, Chemical engineering research & design 72 (1994) 763–776.