

# Methane-bearing shallow gas-charged sediments in the eastern Arabian Sea: a probable source for greenhouse gas

S. M. KARISIDDAIAH\* and M. VEERAYYA\*

(Received 2 December 1992; accepted 9 April 1993)

Abstract—Detailed sub-bottom profiling revealed extensive occurrence of acoustic maskings along the western continental margin of India. These maskings are considered to be methane-rich. A conservative estimate of the potential sub-surface methane in these gas-charged sediments is found to be of the order 2.60 Tg. Further, a rough estimate of the annual total output of methane from the area is found to be 0.039 Tg CH<sub>4</sub>, which may diffuse into the overlying waters in the event of destabilization of this reservoir due to neo-tectonic activity.

### INTRODUCTION

ALTHOUGH oceans are relatively minor source  $(10 \text{ Tg y}^{-1} \text{ or nearly } 2\%$  of total methane emission from an annual flux of 400–600 Tg) of atmospheric methane (CICERONE and OREMLAND, 1988; HOUGHTON *et al.*, 1990; KHALIL and RASMUSSEN, 1990; WANG *et al.*, 1990; FUNG *et al.*, 1991; TAYLOR *et al.*, 1991; MULLER, 1992; STREET-PERROTT, 1992), OWENS *et al.* (1991) reported high concentrations of methane in the Arabian Sea and calculated the flux of methane (0.04 Tg) to the atmosphere up to five times greater than the previously reported average ocean flux. And, their study emphasizes that the magnitude of the methane fluxes from the Arabian Sea and the link with the monsoon suggest that this region may be particularly sensitive to climate change. Further, the world's oceans are a more significant source of methane than is generally believed (HOVLAND and JUDD, 1992). Recently, we have documented the extensive occurrence of acoustic masking along the western continental margin of India (KARISIDDAIAH *et al.*, 1993). Here we present a scenario of the sub-surface methane occurrence and its implications.

Methane is a powerful greenhouse gas (CICERONE and OREMLAND, 1988; HOUGHTON *et al.*, 1990) which plays an important role in atmospheric chemistry by influencing both the ozone concentration and the infrared radiative flux (SVENSSON *et al.*, 1991). Its concentration in the atmosphere is currently increasing globally by about 1% each year (BLAKE and ROWLAND, 1988). For about 10,000 years, the methane concentration remained around 0.7 ppmv. For the last 200 years it has begun rising to the present concentration of about 1.7 ppmv. Methane concentration in the glacial atmosphere was only half that of the pre-industrial Holocene (STAUFFER *et al.*, 1988).

Shallow hydrocarbon gas, mostly methane, has been reported from continental margins worldwide (CLAYPOOL and KVENVOLDEN, 1983; HOVLAND and JUDD, 1988; KVENVOLDEN,

<sup>\*</sup>National Institute of Oceanography, Dona Paula, Goa-403004, India.

1988; DAVIS, 1992; JORGENSEN, 1992). Published data on gas-charged horizons of sediments due to wipeouts, reflector terminations, seeps and acoustic maskings in seismic profiles, side scan sonar records and echograms have been variously reported (BHATTA-CHARYA *et al.*, 1974; KAPLAN, 1974; SCHUBEL, 1974; WATKINS and WORZEL, 1978; MCQUIL-LIN and FANNIN, 1979; CARLSON *et al.*, 1985; BOUMA *et al.*, 1990; AHARON *et al.*, 1992). It is well known that the addition of gaseous phase compounds to the otherwise fluid saturated seafloor sediments alters the acoustic properties of the seafloor (ANDERSON and BRYANT, 1987). Usually the propagation speed of compressional waves through the seafloor is reduced and spatial attenuation rate is increased. Back scattering of acoustic energy is often enhanced. These effects produce readily identifiable anomalies in high-resolution sub-bottom reflection profiles of the shallow seafloor. Further, interstitial methane concentrations as bubbles in a layer of reducing sediment attenuate sound and mask the underlying reflectors (WHITICAR, 1990). The present study describes such acoustic anomalies from the eastern Arabian Sea and their implications.

#### METHODS

Nearly 20,000 line-km of high-resolution seismic reflection profiles were obtained along lines spaced at 20 km intervals, across the western continental shelf of India during various cruises of R.V. *Gaveshani*. A Huntec Hydrosonde M2A (main pulse: 5 kHz), and an ORE sub-bottom profiler (3.5 kHz) were used in conjunction with side scan sonar (EG & G Mark 1B, dual channel recorder: 259-3 and tow fish 272), and Kelvin and Hughes MS-45 echosounder (30 kHz). Positions were obtained using Satellite navigation system (Marconi MA 722).

## **RESULTS AND DISCUSSION**

The area covered by present study is roughly  $0.13 \times 10^6$  km<sup>2</sup> and stretches from Gulf of Kutch in the north to Cochin in the south (Fig. 1). In general, the shelf is widest off Tarapur (345 km) while it narrows down (<60 km) off Cochin. The shelf is characterized by a gently dipping seafloor, with an average gradient of 1:400–1:3000, to a water depth of 140 m. The seafloor is marked by even topography up to 50–60 m water depth and is carpeted by silts and clays, while calcareous sands occur between 50 and 100 m water depths.

Shallow seismic profiling in the inner shelf showed about 5–35 m weakly-stratified acoustically transparent sediments (clays) rarely interrupted by buried rocks and often incised by palaeo-channels of different dimensions (KARISIDDAIAH *et al.*, 1993). Within the clayey sediments sub-bottom is marked by anomalous seismic signatures, here designated as acoustic maskings (Fig. 2), with different shapes ranging from inverted "U" shaped or mushroom type, dome or conical shape, conical and inverted "U" shaped features surfacing above the seafloor, seeps and wipeouts. The presence of these various types are not confined to particular area, as they are often inter-related and sometimes vast stretches of the inner shelf is covered by one of these types only. However, the surfacing type of acoustic maskings are not only restricted to the nearshore sediments but are also noticed on the upper continental slope and often prominent seeps appear in the overlying water column indicating significant contribution of gas from the slope sediments. Sonographs show the presence of these acoustic maskings as indistinct features.

The present study reveals that in the inner shelf the anomalous seismic signatures appear



Fig. 1. Location map of the study area; thickened portion denotes the area where gas-charged sediments are noticed in shallow seismic profiles. Lettered segments indicate locations of seismic records shown in Fig. 2. Inset shows the spatial distribution of stations occupied by OWENS *et al.* (1991) for methane observations in the Arabian Sea.

just a few m below the seafloor (Fig. 2). However, upward migration of hydrocarbon gases by either molecular diffusion or bubble formation and ebullition (SwEENEY, 1988) from these sediments into the overlying waters could be possible. In some places, these anomalous features are seen at the seafloor indicating existence of sufficient pressure in the gas for its escape which has been confirmed by side scan sonar mapping as indistinct bubble vents (KARISIDDAIAH *et al.*, 1993). Often well stratified horizons that contain wipeouts might act as traps for the accumulation of gas.

Oceanic dissolved methane concentrations are normally in excess of atmospheric equilibrium values in surface waters but show a rapid decrease with depth (SCRANTON and BREWER, 1978). Deep North Atlantic waters have only *ca* 30% of their atmospheric equilibrium values of methane and deep North Pacific waters have only *ca* 10%. The studies of OWENS *et al.* (1991) indicated that the methane concentrations in the Arabian Sea varied considerably with depth, being undersaturated, with respect to atmospheric concentrations, below 250 m (Fig. 1, inset). However, much of the water column was supersaturated with methane at depths <200 m (OWENS *et al.*, 1991). Although the possibility of lateral transport of methane produced in shallow water sediments is not proven yet, the presence of conical and dome-shaped methane-bearing acoustic maskings on the shallow seafloor in the eastern Arabian Sea does suggest a significant contributor of hydrocarbon gases to the surrounding waters. The presence of methane in the shelf sediments of the eastern Arabian Sea can also be correlated with phenomena reported elsewhere (EHHALT, 1974; SWINNERTON and LAMONTAGNE, 1974; MARTENS, 1982; FADER, 1991; WARD, 1992).

The formation of gas-charged sediments is due to relatively large fluxes of labile organic carbon to the seabed. The surficial sediments in the study area consist of high (2–4%) organic carbon content which is mainly terrigenous in nature as indicated by high C/N ratios (10–30) (PAROPKARI *et al.*, 1987). This probably reflects higher accumulation rates leading to an increased decomposition rate (WHITICAR, 1990). It is known that in more rapidly accumulating marine sediments with higher organic matter contents bacterial methane formation is common once the dissolved sulfate has been utilized (CLAYPOOL and KAPLAN, 1974). In some instances methane can exceed saturation relative to the interstitial fluids and free gas may result in sediments (WHITICAR, 1990).

A transgression of the sea and submergence of the west coast forests around 9000– 10,000 years before present were documented (NAMBIAR *et al.*, 1991). High accumulation rates  $(0.44 - 0.88 \text{ mm y}^{-1}; \text{NAMBIAR$ *et al.*, 1991) trapped terrestrial organic matter within the inner shelf sediments; and it became the main biogenic gas source. Besides, a humid climate with maximum mangrove vegetation along the west coast has been reported (VAN KAMPO, 1986) around 10,000 years before present. PETITE-MAIRE *et al.* (1991) proposed that past ecological changes in vast tropical areas as one of the factors that contributed to

Fig. 2. High-resolution seismic reflection profile (3.5 kHz) in the eastern Arabian Sea showing: (A) vast stretches of acoustic maskings as inverted "U" shaped features overlain by 25 ms-thick weakly stratified acoustically transparent sediments; well-defined reflector terminations are clearly seen at 28 ms below the scafloor masking the stratified horizons. (B) Sequestered gas maskings characterized by well defined reflector terminations with wipeouts (broken arrows); a depression like feature at the root of these masking indicating the subsidence is discernible. (C) Distinct wipeouts confined to bedding planes. Discontinuity in seismic reflections is conspicuously seen below the wipeout. (D) Characteristic anomalous cone-shaped acoustic masking surfacing on the seafloor.

Arrow indicates acoustic masking. ATC1 = weakly stratified acoustically transparent sediments; ATC2 = stratified acoustically transparent sediments. U = Late Pleistocene (?) unconformity; M = multiple reflector. Vertical scale is two-way travel time (twtt) in ms. (25 ms corresponds to 18.75 m of the sediment.) See Fig. 1 for location.





methane production. These studies emphasize the role of

the global increase-decrease of methane production. These studies emphasize the role of vegetation as the source for the accumulation of methane gas that produces the acoustic anomalies in these sediments.

## Implications of gas-charged sediments

The importance of present day atmospheric methane and its impact on global warming as described earlier, led us to ponder over the existence of methane which is extensively noticed in high-resolution shallow seismic reflection profiles as anomalous signatures (acoustic masking) over the western shelf, as one of the future indicators for the global warming (?). Therefore, the areal extent (Fig. 1) of methane-bearing sediments has been computed at a value of  $\sim 6500 \text{ km}^2$ . Since the acoustic maskings occur to a sub-bottom depth of 10–15 m, an average thickness of 10 m has been utilized for computing methane concentration. Further, the inferences on 5.5 m long sediment core collected from the northernmost part of the study area and the methane analysis in this core have been considered for the estimation of potential methane. An examination of this core showed bubbles at about 3.5 m and fissures below 4 m (SIDDIOUIE et al., 1981). Some of these fissures and bubbles are 2-3 mm long and are estimated to form about 10% of the volume of the sediment. The partial analysis for the hydrocarbons in the core revealed that it contains: methane (CH<sub>4</sub>), 11.15%; pentane, 1.1 ppm; hexane, 1.3 ppm; and heptane, 0.84ppm. Hence the methane concentration is computed considering the following parameters:

- (1) Area occupied by the gas-charged sediments =  $6500 \text{ km}^2$ .
- (2) Average thickness of gas-charged sediments = 10 m.
- (3) Average porosity of gas-charged sediments = 50%.
- (4) Density of methane Potential methane Potential methane Potential methane Potential methane Potential methane Potential methane =  $0.717 \text{ g l}^{-1}$ = Volume of gas-charged sediments × porosity × methane (%) × density of methane. =  $6500 \times 10^{13} \times 0.5 \times 11.15/100 \times 0.717/1000 =$  $2.5982 \times 10^{12} \text{ g}$

# Potential methane content = 2.60 Tg

From these data we estimated that the potential yield of methane is of the order of 2.60 Tg that might have been trapped in the gas-charged sediments of the inner continental shelf off western India.

Recently, HOVLAND and JUDD (1992) made a crude estimate of the net methane flux through the seabed of the petroliferous areas of the northern North Sea based on the following three criteria: (i) areas with macroseepages produce  $26 \text{ g CH}_4 \text{ m}^{-2} \text{ y}^{-1}$ ; (ii) areas with only pockmarks (microseeps) or intermittent ebullition are assumed to maintain flux equal to half of the active flux, i.e. 13 g CH<sub>4</sub> m<sup>-2</sup> y<sup>-1</sup>; and (iii) areas underlain by petroliferous sedimentary rocks, but without pockmarks, produce about half this again: 6 g CH<sub>4</sub> m<sup>-2</sup> y<sup>-1</sup>. Nevertheless, in the absence of any other figure, with the suspicion that all hydrocarbon-rich areas of the world are important and have a net upward methane flux through the seabed, HOVLAND and JUDD (1992) have estimated a global output of methane from the seabed of all continental margin areas down to 250 m water depths. Since the prolific occurrences of acoustic maskings on the shelf off western India, especially off Ratnagiri and Bombay, are confined to oil and gas basinal areas, the third criteria—6 g CH<sub>4</sub> m<sup>-2</sup> y<sup>-1</sup> in the petroliferous areas without pockmarks has been considered for the estimation of methane flux in sub-surface sediments. Therefore, the net methane flux through the seabed of the western shelf is found to be  $0.039 \text{ Tg y}^{-1}$ . A comparison of our estimates (0.039 Tg y<sup>-1</sup>) for a part of the Arabian Sea with the overall methane flux (0.04 Tg y<sup>-1</sup>) to the entire Arabian Sea (OWENS *et al.*, 1991) clearly indicates the presence of an appreciable reservoir of methane in the subsurface gas-charged sediments of the continental shelf. The widespread gassy nature of the continental shelf off western India, therefore, appears to be an important source of methane. However, in all probability, a significant portion of the methane gas would be oxidized before it can escape from the seabed and enter the atmosphere (MECHALAS, 1974; REEBURGH, 1982).

The geophysical studies reveal a well-knit assemblage of NW–SE, NNW–SSE, ENE– WSW, NE–SW and N–S trending lineaments/faults–fractures/fissures on the western continental margin of India (EREMENKO and DUTTA, 1968; NAINI and TALWANI, 1983; BISWAS, 1988; KOLLA and COUMES, 1990; SUBRAHMANYAM *et al.*, 1993). The multichannel seismic reflection data have also revealed several faults within the sediments of the western margin (MURTHY *et al.*, 1981; RAO and SRIVASTAVA, 1981). These tectonic assemblages serve as controlling structural elements in destabilizing the existing methane reservoir that leads to upward diffusion of hidden methane into the overlying waters, in the event of neotectonic activity (GUHA and PADALE, 1981; MISHRA *et al.*, 1989).

Acknowledgements—We thank Dr B.N. Desai, Director, National Institute of Oceanography, for his keen interest and permission to publish the paper; and to Dr R.R. Nair for his critical comments and valuable suggestions to improve the paper. The constructive criticism and useful suggestions offered by two anonymous reviewers have greatly improved the manuscript. We are extremely thankful to Professor R. W. Sternberg, editor, for his valid suggestions.

#### REFERENCES

- AHARON P., E. R. GRABER and H. R. ROBERTS (1992) Dissolved carbon and  $\delta^{13}$ C anomalies in the water column caused by hydrocarbon seeps on the northern Gulf of Mexico slope. *Geo-Marine Letters*, 12, 33-40.
- ANDERSON A. L. and W. R. BRYANT (1987) Distribution of seafloor gas in the northwestern Gulf of Mexico. Proceedings, Nineteenth Annual Offshore Technology Conference, Houston TX, pp. 295–299.
- BHATTACHARYA S. N., S. K. CHAKRABORTI, K. CHANDRA, M. C. GUPTA and M. MATHUR (1974) Gaseous hydrocarbons in the seabottom cores of the Bombay High structure. Oil and Natural Gas Commission Bulletin India, 11, 39–42.
- BLAKE D. R. and F. S. ROWLAND (1988) Continuing worldwide increase in tropospheric methane, 1978–1987. Science, 239, 1129–1131.
- BISWAS S. K. (1988) Structure of the western continental margin of India and related igneous activity. *Geological Society of India Memoir*, **10**, 371–390.
- BOUMA A. H., H. H. ROBERTS and J. M. COLEMAN (1990) Acoustic and geological characteristics of near surface sediments, upper continental slope of northern Gulf of Mexico. *Geo-Marine Letters*. **10**, 200–208.
- CARLSON P. R., M. GOLAN-BAC, H. A. KARL and K. A. KVENVOLDEN (1985) Seismic and geochemical evidence for shallow gas in sediments on Navarin continental margin, Bering Sea. American Association of Petroleum Geologists Bulletin, 69, 422–436.
- CICERONE R. J. and R. S. OREMLAND (1988) Biogeochemical aspects of atmospheric methane. *Global Biogeochemical Cycles*, **2**, 299–327.
- CLAYPOOL G. E. and I. R. KAPLAN (1974) The origin and distribution of methane in marine sediments. In: Natural gases in marine sediments, I. R. KAPLAN, editor, Plenum Press, New York, pp. 99–139.
- CLAYPOOL G. E. and K. A. KVENVOLDEN (1983) Methane and other hydrocarbon gases in marine sediments. Annual Review of Earth Planetary Science Letters, 11, 299–327.
- DAVIS A. M. (1992) Shallow gas: an overview. Continental Shelf Research, 12, 1077-1079.
- EHHALT D. H. (1974) The atmospheric cycle of methane. Tellus, 26, 58-70.

EREMENKO N. A. and A. K. DUTTA (1968) Regional geological framework and evaluation of the petroleum

prospects of the Laccadive Archipelago and the adjoining offshore territory, southwest of India. Oil and Natural Gas Commission Bulletin India, 5, 29–40.

- FADER G. B. J. (1991) Gas-related sedimentary features from the eastern Canadian shelf. Continental Shelf Research, 11, 1123–1153.
- FUNG I., J. JOHN, J. LERNER, E. MATHEWS, M. PRATHER, L. P. STEELE and P. J. FRASER (1991) Three dimensional model synthesis of the global methane cycle. *Journal of Geophysical Research*, 96(D2), 13,033–13,066.
- GUHA S. K. and J. G. PADALE (1981) Seismicity and structure of the Deccan Trap Region. Geological Society of India Memoir, 3, 153–164.
- HOUGHTON J. T., G. J. JENKINS and J. J. EPHRAUMS (1990) Climate change. The IPCC Scientific Assessment. Cambridge University Press, Cambridge, pp. 18–22.
- HOVLAND M. and A. G. JUDD (1988) Seabed pockmarks and seepages. Impact on geology, biology and marine environment, Graham & Trotman, London, 293 pp.
- HOVLAND M. and A. G. JUDD (1992) The global production of methane from shallow submarine sources. Continental Shelf Research, 12, 1231–1238.
- JORGENSEN N. O. (1992) Methane-derived carbonate cementation of marine sedimentation from the Kattegat, Denmark: Geochemical and geological evidence. *Marine Geology*, 103, 1–13.
- KAPLAN I. R. (1974) Introduction. In: Natural Gases in marine sediments, Plenum Press, New York, pp. 1-10.
- KARISIDDAIAH S. M., M. VEERAYYA, K. H. VORA and B. G. WAGLE (1993) Gas-charged sediments in the inner continental shelf off western India. *Marine Geology*, 110, 143–152.
- KHALIL M. A. K. and R. A. RASMUSSEN (1990) Constraints on the global source of methane and an analysis of recent budgets. *Tellus*, 42B, 229–236.
- KOLLA V. and F. COUMES (1990) Extension of structural and tectonic trends from the subcontinent into the castern Arabian Sea. *Marine and Petroleum Geology*, **7**, 188–196.
- KVENVOLDEN K. A. (1988) Methane hydrate—a major reservoir of carbon in the shallow geosphere? *Chemical Geology*, **71**, 41–51.
- MARTENS C. S. (1982) Methane production, consumption and transport in the interstitial waters of coastal marine sediments. In: *The dynamic environment of the ocean floor*, K. A. FANNING and F. T. MANHEIM, editors, Lexington Books, Lexington, MA, pp. 187–202.
- MECHALAS B. J. (1974) Pathways and environmental requirements for biogenic gas production in the Ocean. In: Natural Gases in Marine Sediments, I. R. KAPLAN, editor, Plenum Press, New York, pp. 11–25.
- MCQUILLIN R. and N. FANNIN (1979) Explaining the North Sea's Lunar Floor. New Scientist, 83, 90-92.
- MISHRA D. C., A. P. SINGH and M. B. S. VYAGHRESWARA RAO (1989) Idukki earthquake and the associated tectonics from gravity study. *Journal Geological Society of India*, 34, 147–153.
- MULLER J. F. (1992) Geographic distribution and seasonal variation of surface emissions and deposition velocities of atmospheric trace gases. *Journal of Geophysical Research*, **97**(D4), 3787–3804.
- MURTHY K. V. S., B. N. PRASAD and G. S. RAWAT (1981) Structure of continental margin off Bombay. In: Workshop on geological interpretation of geophysical data, R. P. RAO, editor, Institute of Petroleum Exploration, ONGC, Dehradun, pp. 41–48.
- NAINI B. R. and M. TALWANI (1983) Structural frame work and the evolutionary history of the continental margin of western India. In: *Studies in continental margin geology*, J. S. WATKINS and C. L. DRAKE, editors, American Association of Petroleum Geologists Memoir, 34, 167–191.
- NAMBIAR A. R., G. RAJAGOPALAN and B. R. J. RAO (1991) Radiocarbon dates of sediment cores from inner continental shelf off Karwar, west coast of India. *Current Science*, **61**, 353–354.
- OWENS N. J. P., C. S. LAW, R. F. C. MANTOURA, P. H. BURKILL and C. A. LLEWELLYN (1991) Methane flux to the atmosphere from the Arabian Sea. *Nature*, 354, 293–295.
- PAROPKARJ A. L., CH. M. RAO and P. S. N. MURTY (1987) Environmental controls on the distribution of organic matter in recent sediments of the western continental margin of India. In: *Petroleum geochemistry and exploration in the Afro-Asian Regions*, R. K. KUMAR, P. DWIVEDI, V. BANERJIE and V. GUPTA, editors, Bilkema, Rotterdam, pp. 347-361.
- PETITE-MAIRE N., M. FONTUGNE and C. ROULAND (1991) Atmospheric methane ratio and environmental changes in the Sahara and Sahel during the last 130 kyrs. *Palaeogeography*, *Palaeoclimatology*, *Palaeoecology*, 86, 197–204.
- RAO R. P. and D. C. SRIVASTAVA (1981) Seismic stratigraphy of west Indian offshore. In: Workshop on geological interpretation of geophysical data, R. P. RAO, editor, Institute of Petroleum Exploration, ONGC, Dehradun, pp. 49–57.
- REEBURGH W. S. (1982) A major sink and flux control for methane in marine sediments: anaerobic consumption.

In: The dynamic environment of the ocean floor, K. A. FANNING and F. T. MANHEIM, editors, Lexington Books, Lexington, MA, pp. 203–217.

- SCHUBEL J. H. (1974) Gas bubbles and the acoustically impenetrable, or turbid, character of some estuarine sediments. In: Natural gases in marine sediments, I. R. KAPLAN, editor, Plenum Press, New York, pp. 275– 298.
- SCRANTON M. I. and P. G. BREWER (1978) Consumption of dissolved methane in the deep ocean. Limnology and Oceanography, 23, 1207–1213.
- SIDDIQUIE H. N., D. GOPALA RAO, K. H. VORA and R. S. TOPGI (1981) Acoustic masking in sediments due to gases on the western continental shelf of India. *Marine Geology*, 39, M27–M37.
- STAUFFER B., E. LOCHBRONNER, H. OESCHGER and J. SCHWANDER (1988) Methane concentration in the glacial atmosphere was only half that of the preindustrial Holocene. *Nature*, 332, 812–814.
- STREET-PERROTT F. A. (1992) Tropical wetland sources. Nature, 355, 23-24.
- SUBRAHMANYAM V., M. V. RAMANA and D. GOPALARAO (1993) Reactivation of Precambrian faults on the southwestern continental margin of India: evidence from gravity anomalies. *Tectonophysics*, 219, 327–339.
- SVENSSON B. H., J. C. LANTSHEAR and H. RODHE (1991) Sources and sinks of methane in Sweden. Ambio, 20, 155–160.
- SWEENEY R. E. (1988) Petroleum related hydrocarbon seepage in a Recent North Sea sediment. Chemical Geology, 71, 53-64.
- SWINNERTON J. W. and R. A. LAMONTAGNE (1974) Oceanic distribution of low-molecular weight hydrocarbons base line measurements. *Environmental Science and Technology*, 8, 657–663.
- TAYLOR J. A., G. P. BRASSEUR, P. R. ZIMMERMAN and R. J. CICERONE (1991) A study of the sources and sinks of methane and methyl chloroform using a global three-dimensional Lagrangian tropospheric tracer transport model. *Journal of Geophysical Research*, 96(D2), 3013–3044.
- VAN KAMPO E. (1986) Monsoon fluctuations in two 20,000 yr B. P. Oxygen-isotope/pollen records of southwest India. Quaternary Research, 26, 376–388.
- WANG W. C., G. MOLNAR, M. K. W. KO, S. GOLDENBERG and N. D. SZE (1990) Atmospheric trace gases and global climate: a seasonal model study. *Tellus*, 42B, 149–161.
- WATKINS J. S. and J. L. WORZEL (1978) Serendipity gas seep area, south Texas offshore. American Association of Petroleum Geologists Bulletin, 62, 1067–1074.
- WARD B. B. (1992) The subsurface methane maximum in the southern California Bight. Continental Shelf Research, 12, 735–752.
- WHITICAR M. J. (1990) A geochemical perspective of natural gas and atmospheric methane. Organic Geochemistry, 16, 531-547.