Preliminary studies of carbon isotopic composition methane in marine atmosphere over Arabian Sea

D.Kameswara Rao and R.A.Jani, Physical Research Laboratory, Navarangpura, Ahmedabad, India. e-mail : kamesh@prl.res.in

Introduction :

Methane is naturally occurring and a product of human activities.

Average Methane concentration in the atmosphere is ~1800ppbV

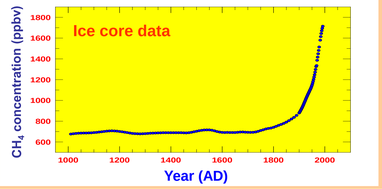
Methane concentration is varied from 800ppbV to 1800ppbV

Air samples were collected during 24th – 28th Nov. 2010

Sample Volume : 70 L (for isotopic analysis)

100cc air samples were Collected for methane Concentration measurements

Location of sampling stations during the Cruise on costal Arabian Sea



This increase has been linked to an increase in population growth & intensified human activities such as fossil fuel use and agriculture.

Table : Details of stations where air samples were collected in Arabian Sea during a cruise in November 2010.

Sr. No	Station code	Latitude	Longitude	Date of Sample collection	Wind direction	Wind Speed (Km/hr)	Distance From coast(Km)
1	SP_1	11°19.25'N	75°34.05'E	24-11-2010	SW	2.5	19.04
2	SP_2	12°51.09'N	74°28.97'E	25-11-2010	Easterly	10	36.22
3	SP_3	13°21.89'N	74°21.89'E	26-11-2010	NE	15	25.91
4	SP_4	14°57.65'N	73°50.20'E	27-11-2010	NE	20-25	22.12
5	SP_5	15°27.32'N	73°30.97'E	28-11-2010	NE	25-30	30.31

Methane Origin

Methane is formed in the earth's interior and at the surface of the earth.

1. **Biogenic Methane :**
   - a) Wetlands
   - b) Paddy fields
   - c) Marine sediments
2. **Thermogenic Methane :** Coal, Petrolem & Natural gas
3. **Biomass burning :**
   - a) Deforestation -- Man made
   - b) Natural fires & Lightning
4. **Volcanoes & Geothermal vents:**

Importance of Isotopic work :

Carbon isotopes proved to be very useful for identification of the different sources of methane. The $\delta^{13}C$ of atmospheric methane can distinguish between CH_4 input from biogenic sources ($\delta^{13}C$ = -60‰), thermogenic sources ($\delta^{13}C$ = -40‰) and biomass sources ($\delta^{13}C$ = -25‰).

$$\delta^{13}C = \left(\frac{(^{13}C/^{12}C)_{sam}}{(^{13}C/^{12}C)_{ref}} - 1 \right) \times 10^3 \ (‰)$$

Objective of this study

To find the source for excess methane in marine atmosphere over costal region of Arabian Sea.

Background of the study

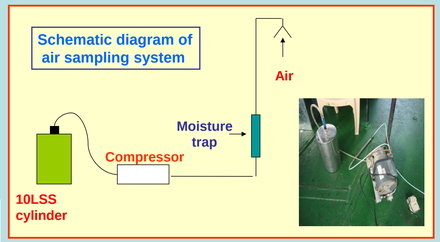
Earlier measurements :

year	CH_4 conc.
1994-95	1690 ± 50 ppbv
2003-07	1730 ± 20 ppbv

No isotopic work was done so far in this region.

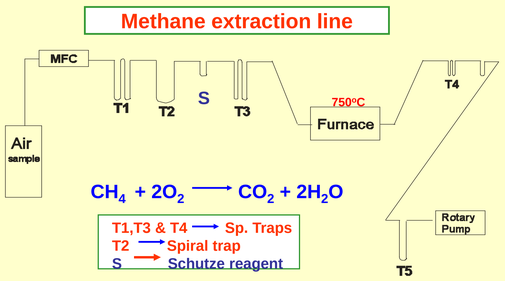
Table : Concentration and $\delta^{13}C$ of methane in atmospheric air samples over costal Arabian Sea

No	Date	CH_4 (ppbv)	$\delta^{13}C$ (‰)
SP_1	24/11/2010	1880±20	-45.9±0.1
SP_2	25/11/2010	1907±30	-45.4±0.1
SP_3	26/11/2010	1893±25	-44.9±0.1
SP_4	27/11/2010	1902±25	-46.5±0.1
SP_5	28/11/2010	1943±30	-46.2±0.1

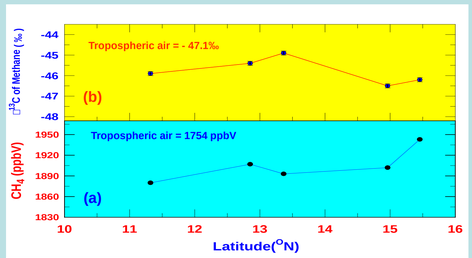


Methane extraction line

Methane extraction line



Rao et al 2008 *Global Biogeochem cycles*



Latitudinal distributions of (a) CH_4 (ppbV) concentration and (b) $\delta^{13}C$ (‰) from the atmospheric air samples collected along the cruise track

It is estimated that an excess methane of ~ 7 to 11% in all these samples.

code	Wind Speed (Km/hr)	CH_4 (ppbV)
SP_3	15	1893±25
SP_4	20 - 25	1902±25
SP_5	25 - 30	1943±30

In these three samples, the Wind direction is NE ie. Wind is blowing from land to sampling location.

The $\delta^{13}C$ of the source can be calculated for each sample separately, using the difference with estimated background values of both concentration and isotopic composition.

$$\delta_S = \frac{(\delta C - C_B \delta_B)}{(C - C_B)}$$

C_B = 1754 ppbV and δ_B = -47.1‰

Calculated $\delta^{13}C$ of Methane source in atmospheric air samples

Code	CH_4 (ppbV)	Excess CH_4 (ppbV)	$\delta^{13}C$ (Measured) (‰)	$\delta^{13}C$ (Calculated) (‰)
SP_1	1880±20	105	-45.9	-30.5
SP_2	1907±30	132	-45.4	-25.4
SP_3	1893±25	118	-44.9	-17.1
SP_4	1902±25	127	-46.5	-37.8
SP_5	1943±30	168	-46.2	-39.4

Inputs of CH_4 in northern latitudes have distinct $\delta^{13}C$ signatures

- −28 to −23‰ ----------→ for boreal forest burning emissions
- −50 to −35‰ ----------→ for natural gas emissions
- −65 to −50‰ ----------→ for CH_4 hydrates
- −69 to −55‰ ----------→ for paddy fields
- −69 to −62‰ ----------→ for wetlands

Conclusion :

Preliminary investigations of isotopic composition of methane in air samples collected in marine atmosphere over coastal Arabian Sea suggests that the excess methane is thermogenic type and probably the methane must have come from land.

Reference :

Rao, D. K., S. K. Bhattacharya, and R. A. Jani (2008). Seasonal variations of carbon isotopic composition of methane from Indian paddy fields, Global Biogeochem. Cycles, 22, GB1004,5 PP,2008, doi:10.1029/2006GB002917.

Acknowledgement :

we are thankful to Prof. R.Ramesh of Physical Research Laboratory, for his encouragement to carry out this project.