Studies of Carbon Isotopic Ratios (δ^{13} C) of Methane in Atmospheric Air Samples from Different Locations in India

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Methane (CH₄) currently has a globally averaged mixing ratio of ~1800 parts per billion by Volume (ppbV) in the troposphere. Its concentration increased from approximately 700 ppbV during the pre-industrial period to about 1800 ppbV today. Between 30 to 40% of CH₄ emissions are from natural origin. The other emissions are related to anthropogenic activity: agriculture, fossil fuel combustion, biomass burning and waste treatment. Removal of CH₄ from the atmosphere is primarily due to oxidation by the hydroxyl radical (OH). A small fraction of the CH₄ is also removed by oxidation in soils. Recent studies indicate that a very small fraction of atmospheric CH₄ is lost in caves. The carbon isotopic composition (δ^{13} C) of CH₄ is useful for constraining the global CH₄ budget and identifying CH₄ sources. This technique is widely used all over the world to identify methane sources, especially in the northern Hemisphere. Very limited work has been done from India in the last decade to measure δ^{13} C of CH₄ in atmospheric air to identify its sources. We present here a summary of the work carried out in the last decade on δ^{13} C of CH₄ in air samples collected from different environments like 1) a high-altitude station (Mt. Abu); 2) inside caves (A.P state); 3) a marine environment (Arabian Sea) and 4) an urban area (Ahmedabad) and discuss its implications. The scientific conclusions are given below.

The values of δ^{13} C of CH₄ in air samples collected from a high-altitude station are enriched compared to that of from tropospheric value (-47.1‰) which indicates that methane is consumed (less than tropospheric value in few samples) due to either biogeochemical process or more interaction with OH radicals. An interesting observation in Billasurgam cave air samples is a decrease in methane concentration from mouth to interior of the cave. As the sampling location is closed further and hence the ventilation is poor, it clearly implies that the carbon from CH₄ is being consumed by the methanotrophic bacteria in the interior of the cave and creating a concentration gradient which is seen in the results. The values of δ^{13} C of CH₄ in air samples collected from coastal area of Arabian Sea are enriched compared to the tropospheric values (-47.1‰) which indicates that the excess methane(~ 9%) is thermogenic type and probably from land. The data from an urban area (Figure 1) suggests that two dominant sources (automobile exhaust and natural gas leakage) contribute during night time. Both the sources have equal contribution from 21:00 to 6:00 where as automobile exhaust dominates after 6:00 hours.



Figure 1. Diurnal cycle of CH₄ ppmV mixing ratio and δ^{13} C (‰) in Ahmedabad city during 11-12th June 2003.