Methane, Hydroxyl, and the Self-cleaning Capacity of the Atmosphere

Abstract:

Solar ultraviolet (UV) radiation energizes atmospheric photo-chemistry by generating highly reactive molecular fragments, the hydroxyl radicals (OH). These OH radicals are effective cleaning agents of the atmosphere as they oxidize many reduced compounds emitted by the biosphere and its humans. The greenhouse gas methane (CH₄) is one of these compounds, and its atmospheric mixing ratio has tripled in the last 200 years, having been nearly constant for the previous ½ million. The reaction OH+CH₄→CH₃+H₂O limits the atmospheric residence time of CH₄ to about 10 years, but with a range of 7-14 years predicted by different models. The strength of this cleaning mechanism is limited and is only effective if the emissions of species to be removed (e.g., CO, CH₄) do not exceed certain thresholds, beyond which OH would fall to low values and allow CH₄ runaway with catastrophic consequences for climate. Catalytic regeneration of OH by nitrogen oxides (NOx) appears key to maintaining a vigorous oxidative capacity. Natural sources of NOx, mostly from lightning, soils, and forest fires, probably already had a key role in preventing CH₄ runaways over geological history. A tripling of NOx emissions since pre-industrial times likely increased OH further, while concurrent increases in CH₄ (as well as CO and other hydrocarbons) should have suppressed it – with the net change in OH uncertain to the present and into the future. Models should be evaluated with both local (in-situ) and global (satellite) observations and used to simulate future OH for different scenarios, e.g., where NOx emissions decrease while those of CH₄ continue to rise.

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