Limits to the Photochemical Chemical Stability of the Troposphere: The Importance of Natural Emissions of Nitrogen Oxides in Preventing Runaway Growth of Atmospheric Methane

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The biosphere, with its human component, emits numerous chemicals to the atmosphere including about 3 Gtons of reduced carbon in the form of carbon monoxide (CO), methane (CH_4) and other volatile organic compounds (VOCs), as well as various nitrogen, sulfur, and halogen species. Their removal from the atmosphere is currently dominated by photo-chemical oxidation reactions that convert the emitted species to more soluble forms which are then easily removed by deposition (wet or dry) to the Earth's surface. The strength of this photo-oxidation is limited and is only effective if the species to be removed (e.g. CH_4) do not exceed certain thresholds. A critical role is played by nitrogen oxides (NOx), which although emitted in relatively small amounts by natural processes such as forest fires and lightning, catalyze the production of photo-oxidants (e.g., the hydroxyl radical, OH) that react with CH_4 and other emitted species. Near the thresholds, the chemical system displays highly non-linear features including multiple steady states, internally generated oscillations, and period-doubling transitions to chaos. Collapse of the Earth's oxidizing capacity would likely result in strong greenhouse warming from the large increase in atmospheric CH_4, but it is unclear if this has actually occurred over geological history.