

Air Pollution and Tropospheric Processes

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Biogenic Hydrocarbons: Interaction Between Air Pollution and Terrestrial Ecosystems

Nonmethane hydrocarbons (NMHCs) play an important role in the atmosphere. Photochemical oxidation of hydrocarbons leads to ozone (O₃), organic acid, and carbon dioxide (CO₂) production, with major implications for local and regional air quality, acid deposition, and the greenhouse effect. In addition, emissions of atmospheric NMHCs lead to an increased aerosol loading, which has major implications for the global heat budget, human health, tropospheric chemistry, and visibility.

The most important anthropogenic sources of hydrocarbons include fossil fuel combustion, direct release from industry, industrial processing of chemicals, and waste. Globally, the estimated anthropogenic NMHC emission rate is about 10¹⁴ g per year. Biological processes in both marine and terrestrial environments contribute to biogenic hydrocarbon sources. For the terrestrial biosphere, the principal hydrocarbon sources come from vegetation. In regions such as eastern Northern America, the biogenic hydrocarbon emission rate exceeds that of anthropogenic emissions. On the global scale, it is estimated that vegetation emits about 10¹⁵ g per year, an amount that is comparable to the global methane emission.

Plants product a variety of hydrocarbons, including isoprene (~51%), terpenes (~31%) oxygenated organics (~16.2%), alkenes (~2%), and methanol (~0.22%). Hence, isoprene (2-methyl-1,3-butadiene, CH₂=C(CH₃)CH=CH₂) is one of the most abundant hydrocarbons emitted from the terrestrial biosphere, with a global averaged production rate of about 600 Tg yr⁻¹. Many deciduous trees emit about 1% of the CO₂ that they fix as isoprene. The biogenic isoprene comprises a hydrocarbon source that exceeds the emission of the nonmethane hydrocarbons of anthropogenic origin. The biochemical pathways in the synthesis of the common biogenic hydrocarbons such as isoprene and monoterpenes share a common precursor compound, dimethylallyl pyrophosphate (DMAPP). It is appear that a membrane-bound, light-activated enzyme catalyzes the elimination of pyrophosphate from DMAPP. As a result, both the leaf temperature and the solar photon flux control the isoprene emission rate.

Isoprene is chemically very reactive to influence oxidation levels over large portions of the continental troposphere. Atmospheric oxidation reactions of isoprene are initiated by attack from the hydroxyl radical OH, ozone O₃, or the nitrate radical NO₃. Since isoprene is emitted from vegetation only during daylight hours, the reaction with OH is expected to be the dominant tropospheric removal pathway for isoprene. The reaction between isoprene and OH occurs almost entirely by OH addition to the >C=C< bonds, yielding a thermodynamically favored hydroxyallylic radical. Under atmospheric conditions, this radical reacts primarily with oxygen molecules to form hydroxyalkyl peroxy radicals. Subsequently, the reaction between the peroxy radical and NO leads to the formation of hydroxyalkoxy radicals. The dominant tropospheric

reaction of hydroxyalkoxy radicals is believed to be decomposition, leading to the formation of various oxygenated and nitrated organic compounds.

At present, however, information concerning the detailed mechanism and pathways of the oxidation isoprene reactions is very limited. In particular, there is a little information available on the chemistry of the radical intermediates of isoprene oxidation reactions. Our understanding of the atmospheric oxidation mechanism of isoprene is primarily based on a series of environmental chamber investigations to identify the final reaction products. Hence there is a need for future research for chemical kinetics and mechanism of the isoprene oxidation reactions.

Biogenic NMHCs also constitute an important fraction of total volatile organic compounds (VOCs) in the urban and regional environments. Oxidation of the atmospheric VOCs results in the formation of organic peroxy radicals that facilitate the cycling of NO to NO₂, a process directly responsible for ozone formation. Hence biogenic NMHCs have major implications for urban and regional air pollution. On the other hand, air pollution can also have a major impact on the biosphere. For isoprene, the chemical lifetime of isoprene due to oxidation by OH, O₃, and nitrate radicals are about 1.7, 31, and 0.8 hours, respectively. This implies that isoprene will be quickly oxidized once being released into the atmosphere. In the case of efficient transport of NO_x from anthropogenic sources into a forest region, the coupling between VOCs and NO_x will result in elevated ozone concentrations. Ozone is known to have a great damage potential for the biosphere. Ozone diffuses into the foliage through the stomata and attacks cell membranes, impacting the respiration rate of the plant and reducing the rate of photosynthesis and uptake of carbon from the atmosphere. Hence, one of the major research agendas associated with the global climate and environment changes is to understand the interaction between air pollution and terrestrial ecosystems.

Lightning Impacts on Atmospheric Chemistry and Global Climate and Environment Changes

Lightning is a very common electrical phenomenon in the atmosphere. It is estimated that 60-100 lightning strokes occur in every second globally. Lightning produces nitrogen oxides and, therefore, has major implications on atmospheric chemistry. NO_x production by lightning has been a subject of numerous investigations. However, estimate of global NO_x production by lightning varies considerable, with a major uncertainty. To estimate the global emission of NO_x by lightning, several parameters needed to be defined, including the production rate of NO_x by lightning and global distribution of lightning.

We have estimated the global NO_x production by lightning using the global lightning observation from the Optical Transient Detector (OTD). OTD was launched in 1995 into an orbit of 750 km with an inclination of 70 degrees, therefore covering 70S to 70N. We have employed the OTD data to derive the seasonal and global distribution of lightning, to estimate global NO_x production by lightning, yielding a value about 8 to 10 Tg/year. This emission rate is only slightly smaller than the estimated Nox emission from the anthropogenic sources (~21 Tg/year based on the data from the Global Emission Inventory Activity GEIA). Hence, lightning contributes significantly to the total emission of NO_x on the global scale.

In addition, we have performed sensitivity studies using a global chemical transport

model (MOZART) to constrain the global NO_x emission rate by lightning. Comparison of the model results with NO_x measurements obtained from field campaigns indicated that 7 Tg/year NO formation uniformly and vertically distributed in the cloud or 3 Tg/year distributed in the upper region of clouds produced better agreement with the observations. In addition, the model calculations suggest that NO_x enhancement by lightning is limited only to the upper troposphere in the tropics, but NO_y enhancement by lightning is more prominent. Recycling of NO_x from lightning enhanced HNO_3 and PAN provides additional sources of NO_x oceans in the tropics.

The lightning activity may also have a profound connection with the global environmental and climate changes. First, it is anticipated that there will be enhanced lightning activity due to global warming. In addition, there appears to have a changing lightning characteristics due to air pollution, i.e., increasing air pollutants and aerosol loading. A recent study has shown that there is an increased positive cloud-to-ground lightning discharge due to a recent forest fire occurred in Mexico. A latest analysis of lightning data over the continental US also indicates an increased lightning flash density over urban cities. Hence future studies are required to study the interaction between lightning and air pollution, and subsequently the lightning impacts on the atmospheric chemistry.