The Long Reach of Biogenic Emissions in the Atmosphere

Sanford Sillman

Abstract This chapter provides a brief summary of the impacts of biogenic emissions in the atmosphere, focusing on reactive organics. These species have a significant impact on the chemical balance of the troposphere and also affect the formation of ozone and other secondary species in polluted regions. Methane, though slowly reacting, also plays an important role in the chemistry of the global troposphere. Methane and aerosol production from biogenic organics both affect climate. Two distinctions are emphasized: (i) between naturally occurring emissions from largely unperturbed ecosystems (usually forests) as opposed to emissions associated with agriculture and other human activities; and (ii) between reactive emissions (including slowly reacting species) and completely nonreactive species such as carbon dioxide. The reactive species are eventually removed from the atmosphere, but carbon dioxide and other nonreactive species accumulate in the atmosphere over time and are only removed on time scales of 100 years or longer.

It is widely known that emissions from the biosphere have a large effect on the evolution of the atmosphere. Most immediately, respiration of CO_2 and exhale of O_2 by plants causes a noticeable seasonal atmospheric cycle, with CO_2 decreasing during the northern summer at the time of maximum net photosynthesis on a global scale. In addition to the global cycle, the biosphere represents a reservoir of carbon that can be exchanged with atmospheric CO_2, with time scales ranging from years (for most plant species) to centuries (for stored carbon in soils). On geologic time scales the evolution of the biosphere is directly associated with release of free oxygen (O_2) to the atmosphere, and even today the reservoir of atmospheric oxygen turns over on a time scale of approximately 25 million years. The increase in atmospheric

---

S. Sillman (✉)
Department of Atmospheric, Oceanic and Space Sciences,
University of Michigan, Ann Arbor, MI 48109-2143, USA
e-mail: sillman@umich.edu

T. Fenning (ed.), *Challenges and Opportunities for the World's Forests in the 21st Century*, Forestry Sciences 81, DOI 10.1007/978-94-007-7076-8_32,
© Springer Science+Business Media Dordrecht 2014

oxygen over geologic time (from <0.1 % in the early Earth to approximately 13 % at the start of the Cambrian era and 21 % today) was associated initially with the breakdown of H_2O to form free oxygen and subsequently (including the current long-term cycling of O_2) with the conversion of sulfate and carbonate rocks to organic plant matter.

Over the past 30 years there has been renewed interest in the release of shorter-lived chemically reactive species from the biosphere and its impact on the photochemical balance of the atmosphere. The reactive species include reactive nitrogen (NO and NO_2, collectively known as NO_x) and a range of biogenic hydrocarbons, each with reaction time scales of a few hours in the atmosphere. These species (NO_x and reactive organics) are generally associated with the chemistry of air pollution. The initial studies of the chemistry of polluted air in Los Angeles in the 1950s identified reactions of organics and NO_x that lead to the formation of ozone (O_3), and the reaction sequences identified at that time remain central to the chemistry of polluted environments today. Beginning in the late 1970s it was found that analogous organics are released into the atmosphere by trees, a discovery that received a brief burst of publicity during the 1980 U.S. presidential campaign. These biogenic emissions have a major role in the photochemistry of the atmosphere in remote locations and on global scales. In the late 1980s it was also discovered that biogenic emissions also affected the formation of ozone in polluted regions and that accounting for these emissions had a major impact on the selection of control strategies for ozone. There is still considerable uncertainty about the photochemical breakdown of biogenic organics in the atmosphere, its impact on ozone and reactive nitrogen, and its role in producing organic aerosols. Biogenic emissions also are a major source of atmospheric methane (CH_4), which, although it reacts relatively slowly (on a time scale 9–14 years), is one of the main factors in the photochemistry of the global troposphere. Biogenically produced methane and organic aerosols both have a large impact on the transfer of radiation in the atmosphere. These have a significant impact on climate and are of special concern for their possible impact on climate change today.

In analyzing biogenic emissions it is useful to make a distinction between ***naturally occurring*** emissions that are part of the natural ecosystems and the more general category of biogenic emissions. The term ‘biogenic emissions’ is often regarded as naturally occurring and unrelated to human activities, as opposed to anthropogenic, or human-related emissions. However, the term is also used to refer to emission of species (such as NO_x and methane) that are biological in origin but associated largely with human agriculture and animal husbandry and are strongly influenced by specific practices such as fertilization. A more important distinction is that between naturally occurring emissions, which I will define as emissions from biological organisms in naturally occurring and relatively unperturbed ecosystems, and anthropogenic emissions, which include emissions associated with agricultural practices and other artificial or semi-artificial ecosystems as well as activities related to modern industry and technology. Even this distinction is not absolute: emissions from naturally occurring ecosystems (forests, natural wetlands) are also impacted by the global extent of those ecosystems (which is heavily influenced by human activities) and changes associated with runoff of fertilizer and waste generated by human activities, atmospheric pollution, acid deposition and so on.)

Another important distinction for biogenic emissions involves the time scale. Species are regarded as ***fast-reacting*** (or ***reactive***) if they react on time scales from approximately 10 min to 10 days. Aerosols and semivolatile species (which partition between gas-phase and aerosol components) are also removed from the atmosphere (via surface deposition and usually also by wet deposition during rain events) on a time scale of 5–10 days even if the species are completely nonreactive. The fast-reacting species may be contrasted with ***slow-reacting*** gaseous species such as carbon monoxide (CO) and CH_4, which have atmospheric lifetimes ranging from 2 months (CO) to 14 years (CH_4) with respect to photochemical removal. Finally, special attention must be given to emitted species that are effectively ***nonreactive***, including CO_2 and the original chloro-fluorocarbons (CFC's). There are no immediate removal processes for these species in the troposphere. They participate in global cycles with effective time scales ranging from 75 years (CFCs) to several thousand years or more (CO_2). These nonreactive species have almost no impact in the immediate vicinity of the emission source, but they are associated with some of the most difficult and intractable environmental problems. These are the major drivers of climate change.

The time scale for reactive species also translates directly into a spatial scale of influence. Fast-reacting species often have a large influence on local atmospheric chemistry and are important in the development of ***urban-scale*** pollution evens (with spatial extent approximately 100 km) and ***regional-scale*** pollution events (with spatial scale 1,000 km). Biogenic emissions are especially important for regional events because the latter include a combination of emissions from rural environments (possibly including agriculture, naturally occurring forest ecosystems and wooded suburbs) in combination with on-site and transported emissions from anthropogenic sources. These urban and region-wide pollution events can persist for several days and have detrimental impacts on human health, agricultural productivity and forest ecosystems.

The other major spatial scale for atmospheric pollution involves the ***global-scale*** chemistry for the troposphere as a whole. The global tropospheric balance is dominated by chemistry in remote locations, over oceans and in the 'free troposphere' – which refers to the troposphere above 3,000 m, where the air is generally not in direct contact with surface emissions. The circulation of the atmosphere results in transport and distribution of surface emission sources throughout the troposphere, but the time scales for transport is usually 1 month or more. Chemical balances in the remote troposphere are strongly influenced by two slow-reacting species: carbon monoxide (CO, with atmospheric lifetime 2 months) and methane (CH_4, with lifetime 9–14 years). The fast-reacting species are present in the remote troposphere at much lower concentrations relative to near-source locations, but some fast-reacting species (notably, reactive nitrogen) have a major influence on remote chemistry despite the lower concentrations. Whereas the urban and regional-scale chemistry in polluted regions has an immediate effect in terms of human health and agriculture/ecology, the global-scale processes can affect longer-term atmospheric balances relating to climate. This difference is related to the time scale of months or years (global scale) as opposed to a time scale of days (urban and regional-scale).

The most critical distinction to make with regard to time scale for atmospheric processes is the distinction between these relatively tractable processes (urban, regional or global scale, with temporal response scales from days up to 10 years) and semi-permanent processes that involve long-term changes on a temporal scale that equals or exceeds the human lifespan. The most important long-term species is CO_2, which is also the principal driver of climate change. CO_2 cycles between four major reservoirs – the atmosphere, the biosphere, soils and the surface ocean (to a depth of 100 m) on time scales of a few years, and the biosphere, soil and surface ocean have magnitudes comparable to the atmosphere as reservoirs of atmospheric carbon (which includes both CO_2 and organic carbon in the biosphere which is readily converted to CO_2). However, the only way to remove carbon from these four reservoirs taken as a whole is through transport to the deep ocean, which is a much larger carbon reservoir than the atmosphere or biosphere. Transfer of carbon to the deep ocean (which is associated with the decay of organic matter that has fallen from the near-surface ocean ecosystem) occurs on a time scale of 1,000 years or longer and provides the ultimate sink for CO_2 released from fossil fuels. On shorter time scales little can be done to reduce the levels of atmospheric CO_2 or eliminate the excess carbon that results from fossil fuel usage.

For this reason, the problem of atmospheric CO_2 must be considered in a separate category from other anthropogenic impacts, even though other species also contribute to climate change. The other species that impact climate (most notably methane, black carbon and other aerosols) have atmospheric lifetimes ranging from a few months up to 14 years. These are all short-term in comparison to CO_2. The other species are also less central to modern human activity and lifestyles than CO_2, which unavoidably emitted by the burning of any fossil fuel.

The more reactive species, in contrast to CO_2, are more likely to have immediate rather than long-term impacts. Also in contrast to CO_2, the reactive emissions and their products (primarily ozone and aerosols) have a direct impact on human health and agricultural productivity. These effects are reversible: atmospheric conditions will change in response to changes in emissions. Again, in contrast to CO_2: the impact of reactive emissions reflects the current state of emissions rather than the cumulative total since the beginning of the industrial era. Because the immediate impacts are felt locally, they are more likely to elicit an effective response that addresses the problem.

The major reactive biogenic emissions are as follows:

- **Reactive organics**: The largest organic emissions are isoprene (C_5H_8) and terpenes such as α-pinene ($C_{10}H_{10}$). Both of these are naturally emitted from forests. Isoprene is emitted primarily by oak and other deciduous trees, while the terpenes are emitted primarily by conifers. These are short-lived species (with lifetimes 30 min-2 h), but they lead to complex sequences of reactions that may include long-lived products.
- **Methane (CH_4)**: Methane is associated with a variety of natural emissions (associated primarily with bacterial processes in wetlands) and from a variety of human agricultural activities (most notably, digestion in cattle and other

ruminants and anaerobic decomposition associated with rice cultivation). There are also significant anthropogenic sources, including emissions associated with natural gas production and emission from landfills. A common feature of many biogenic sources of methane is production under anaerobic conditions. In contrast to the reactive organics, methane is long-lived (9–14 years). Due to its long lifetime methane is fairly uniformly distributed throughout the troposphere. Methane is a major factor in the chemistry of the remote troposphere, especially in the mid – and upper troposphere (where there is little direct contact with surface emissions).

- **Nitrogen oxides** (**NO and NO_2, or NO_x**): These emissions are mainly associated with agricultural fertilizers. NO_x is short-lived (2–4 h) but plays central role in the chemistry of the troposphere, so that even a small amount in remote locations and in the mid – and upper troposphere can have a large impact.
- **Nitrous oxide** (**N_2O**): In contrast to the nitrogen oxides, nitrous oxide is a non-reactive species. Its long lifetime in the atmosphere (120 years) makes it more comparable to CO_2 than to the reactive (even slow-reacting) emissions. N_2O is emitted from aerobic bacterial processes in soil, a process that is enhanced by agricultural fertilizers. Once in the atmosphere N_2O accumulates until it reaches the stratosphere, where it is photolyzed by ultraviolet radiation to form NO and NO_2. The resulting nitrogen oxides are an important source for the upper troposphere. Nitrous oxide is a greenhouse gas, and its total contribution to the greenhouse effect is comparable to methane and approximately one-third that of carbon dioxide. Nitrous oxide in the atmosphere has increased since pre-industrial times, but only by 16 %, which is far less than the increase in CO_2 (50 %). The contribution to climate change associated with the increase in N_2O since preindustrial times is therefore an order of magnitude lower than the impact of the increase in CO_2.

The nitrogen oxides have a major impact on the chemistry of the troposphere. Sources include both natural (biogenic N_2O and NO_x created by lightning) and anthropogenic emissions (primarily from automobiles and coal-fired industry and power plants).

The biogenic hydrocarbons are noteworthy because global emissions (primarily isoprene) account for approximately 70 % of total emission of reactive organics. As such, the biogenic species have a large impact on the chemistry of the remote troposphere. Chemistry at remote forest sites is often dominated by just two species: isoprene and NOx. At unperturbed sites NO_x is very low (100 ppt or less) and the resulting chemistry does not create dangerous reaction products and may even cause a decrease in harmful atmospheric ozone. However, a moderate input of anthropogenic NO_x can result in significant photochemical production of ozone. These conditions occur widely in the eastern and southeastern US, where the combination of biogenic isoprene and NO_x (the latter being emitted in large quantities from coal-fired power plants) contributes significantly to ozone production in region-wide pollution events. Similar problems could occur in tropical forested regions as modernizing economic conditions lead to increased NO_x emissions (Fig. 1).

Fig. 1 The Sammis power plant, Steubenville, Ohio. Nitrogen oxides from coal-fired power plants and other anthropogenic sources, in combination with natural emissions of isoprene from deciduous forests, result in ozone formation and are a major contributor to ozone air pollution in the eastern U.S. Government regulation lead to a reduction in nitrogen oxide emissions in the early 2000s, leading to a significant reduction in ozone (http://www.eenews.net/assets/2012/02/08/photo_cw_02.jpg, http://www.eenews.net/public/climatewire/2012/02/08/1)

Ironically, the most important result pertaining to isoprene is its impact on pollution episodes in urban areas. The initial studies of urban smog in the 1950s focused on anthropogenic organic emissions and their role in the formation of ozone during pollution events. Isoprene emissions typically represent just 10 % of total organic emissions in urban locations, although their impact on the chemistry of smog events is enhanced by the rapid rate of reaction of both isoprene and many of its reaction products. In 1988 it was found that when isoprene was included in models for urban pollution formation, results suggested that reductions in emissions of anthropogenic hydrocarbons would be much less effective as a strategy for lowering ozone. These findings were amplified in the 1990s in a series of studies suggesting that in most of the eastern US meaningful reductions in ozone could only be achieved if there were reductions of NOx emissions. At the time major efforts had been launched to reduce emission of anthropogenics, but there was little change in atmospheric ozone. As the role of biogenic hydrocarbons was recognized, policy initiatives shifted to place greater emphasis on reductions of NO_x emissions. The shift to focus on NOx was largely credited for leading to reduced ozone in the eastern U.S. in the 2000s.

Isoprene contributes to issues of atmospheric composition and air quality in four distinct ways. It affects urban air quality directly, largely by determining whether rates of ozone formation in urban locations are sensitive to anthropogenic hydrocarbon emissions, NO_x, or both. It enhances ozone formation in rural areas, which is a function of available NO_x. It is also a dominant factor in the chemistry of air in remote forested regions where NO_x is very low. Lastly, isoprene is a significant atmospheric

Fig. 2 Haze over the Smoky Mountains, Tennessee. A characteristic "blue haze" can be formed by aerosols produced from terpenes, which are emitted from a variety of fragrant plants and especially from coniferous forests. However, today the main constituents of haze, even in the Smoky Mountains, are anthropogenically produced sulfate and nitrate aerosols http://wncmountainliving.blogspot.com/2010/07/blue-haze-on-mountains.html

source of carbon monoxide (CO), which has a long enough lifetime (2 months) to be widely distributed in the troposphere and participate in global-scale chemistry.

Other biogenic organic emissions (primarily terpenes, emitted largely by conifers) can lead directly to aerosol formation. The resulting "blue haze" can be entirely biogenic, although its formation is influenced by the presence of nitrogen oxides. The naturally occurring aerosols may be overshadowed locally by aerosols from anthropogenic sources (Fig. 2).

There is currently a large uncertainty about the impact of isoprene at the global scale, especially with regard to aerosols. The immediate photochemical reaction products of isoprene are all short-lived, like isoprene itself. However some of the subsequent products have lifetimes of a few days or more, long enough to influence chemistry through much of the troposphere. At the same time there is uncertainty about the sources of organic aerosols in the atmosphere. The aerosols are important because they have a detrimental impact on human health and because they have a complex influence on climate. It is known that some aerosols (sulfates) have a significant cooling effect on climate, while others (soot, or black carbon) have a major warming effect by blocking outgoing radiation. Aerosols also affect cloud reflectivity and cloud formation rates, each of which has climate implications. The organic aerosols add an additional level of complexity because it is not clear to what extent

Fig. 3 Rice paddies in Indonesia. Human agricultural activities (primarily rice cultivation and the raising of cattle and other ruminants) represent approximately 25 % of global methane emissions, and the expansion of agriculture (along with other anthropogenic activities) has contributed to a more-than-doubling of the concentration of methane in the atmosphere over the past 200 years (http://media.web.britannica.com/eb-media/97/20297-004-73911B76.jpg)

these species are sensitive to anthropogenic or biogenic emissions. The various isoprene reaction products (the peroxides in particular) are currently being investigated as possible sources of organic aerosols.

Methane also has impacts on local pollution effects and on the global scale, but in a different way from isoprene. Because it reacts slowly, methane has no direct impact on formation of pollutants during urban or regional-scale episodes. Instead, methane is distributed fairly uniformly throughout the troposphere, where it has a major impact on chemistry. This does not mean that methane has no impact on pollution events, however. It has been argued that controlling methane is a cost-effective strategy for reducing ozone. By reducing the global 'background' ozone, a reduction in methane would simultaneously lower ozone in cities and polluted regions around the world. The practical difficulty is that controls on methane can only be put into effect through international agreements. Methane is an important greenhouse gas, and emission reductions are being sought primarily for their impact on climate (Fig. 3).

The major uncertainties for methane are related less to its behavior in the atmosphere than to the possibility of large releases of stored methane as a result of climate change Concern has focused on methane releases from permafrost in response to warming, and also on releases from the continental shelves of oceans. This could have the effect of hastening climate change and of increasing ozone worldwide (Fig. 4).

A final topic worth considering is the stability of the atmospheric cycling of biogenics with respect to chemistry. Some of the most difficult environmental problems involve unstable systems that might suddenly transform to a different mode of

Fig. 4 The Lena River delta in northeastern Siberia. Natural emissions from wetlands associated with anaerobic bacteria is responsible for approximately 40 % of methane emissions to the atmosphere. It is uncertain how climate change will affect emissions from high-latitude wetlands and permafrost (http://www.awi.de/fileadmin/user_upload/News/Press_Releases/2010/2._Quartal_2010/2007_Eispolygone_KPiel_out_p.jpg, http://www.awi.de/en/news/press_releases/detail/item/higher_wetland_methane_emissions_caused_by_climate_warming_40000_years_ago/?cHash=54bc4b14397e0ae4778c9dd7b0d20c80

behavior, often associated with runaway feedback cycles. Climate in general has unstable features: soil moisture and rainfall, snow cover and temperature are each coupled and reinforce each other. The chemistry of both isoprene and methane also involves positive feedback that amplifies the impact of changes in emissions, but there are also factors that are likely to insure stability.

Tropospheric chemistry is controlled largely by the OH radical, which initiates reaction sequences that convert organics (including isoprene and methane) to oxidized forms (ultimately CO and CO_2). At the same time, isoprene (in forest environments) and methane (in the larger free troposphere) act as major sinks of OH, so that increased emissions leads to reduced OH and longer atmospheric lifetimes for themselves. In the case of isoprene, it sometimes happens that local emissions exceed the source of OH, causing a large increase in chemical lifetimes and increased atmospheric concentrations by a factor of five or more. These large increases usually happen in forests dominated by oak, which are high emitters of isoprene. These localized events have little impact on the troposphere as a whole, since the excess isoprene is rapidly removed once it is dispersed beyond the immediate forest environment. Positive feedback on the global scale is important for methane, which (along with CO) represents a large sink for OH in the troposphere as a whole. The direct removal rate for methane through reaction with OH implies a lifetime of approximately 9 years based on ambient OH concentrations. When the removal rate for methane is calculated using complete representation of tropospheric chemistry, including the decrease in concentrations of OH resulting from an increase in methane, the lifetime of methane increased to 14 years.

There is little danger of a major shift in the atmospheric response to increases in isoprene or methane emissions because of many stabilizing features associated with OH chemistry. OH is created partly through photolysis of ozone followed by reaction with water vapor, a process that is not likely to change significantly. The reactions that remove isoprene and CH_4 often regenerate OH and subsequent reaction products are often an additional source of OH. This provides a level of stability to tropospheric chemistry that, sadly, is lacking in other issues relating to climate and atmospheric composition.

Changes in anthropogenic emissions and in biogenics associated with human activities, in combination with naturally occurring biogenic emissions, may affect air quality and impact human health, agricultural productivity and ecosystems. But these are gradual rather than catastrophic changes, and respond relatively rapidly to changes in human practices. The same cannot be said of many other challenges associated with the atmosphere and climate.

Acknowledgments This article is based on research activities supported by the National Science Foundation (grant #ATM-0454838), Environmental Protection Agency (STAR grant #R8333770) and by the University of Michigan. This article has not been subjected to peer and administrative review by either NSF or EPA, and therefore may not necessarily reflect the views of the agencies, and no official endorsement should be inferred.

References and Further Reading

Bloomer BJ, Stehr JW, Piety CA, Salawitch RJ, Dickerson RR (2009) Observed relationships of ozone air pollution with temperature and emissions. Geophys Res Lett 36:L09803. doi:10.1029/2009GL037308

Chameides WL, Lindsay RW, Richardson J, Kiang CS (1988) The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study. Science 241:1473–1474

Dentener FJ, Krol MC (2002) Stability of tropospheric hydroxyl chemistry. J Geophys Res 107(D23):4715. doi:10.1029/2002JD002272

Fiore AM, Jacob DJ, Logan JA, Yin JH (1998) Long-term trends in ground level ozone over the contiguous United States, 1980–1995. J Geophys Res 103:1471–1480

Fiore AM, Jacob DJ, Field BD, Streets DG, Fernandes SD, Jang C (2002) Linking ozone pollution and climate change: the case for controlling methane. Geophys Res Lett 29(19):1919. doi:101.1029/2002GL015601

Forster P, Ramaswamy V, Artaxo P, Berntsen T, Betts R, Fahey DW, Haywood J, Lean J, Lowe DC, Myhre G, Nganga J, Prinn R, Raga G, Schulz M, Van Dorland R (2007) Changes in atmospheric constituents and in radiative forcing. In: Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, Tignor M, Miller HL (eds) Climate change 2007: the physical science basis. Contribution of working group I to the fourth assessment report of the intergovernmental panel on climate change. Cambridge University Press, Cambridge, UK/New York

Frost GJ et al (2006) Effects of changing power plant NOx emissions on ozone in the eastern United States: proof of concept. J Geophys Res 111:D12306. doi:10.1029/2005JD006354

Harvey LDD, Huang Z (1995) Evaluation of the potential impact of methane clathrate destabilization on future global warming. J Geophys Res 100(D2):2905–2926. doi:10.1029/94JD02829

Ito A, Sillman S, Penner JE (2009) Global chemical transport model study of ozone response to changes in chemical kinetics and biogenic volatile organic compounds emissions due to increasing temperatures: Sensitivities to isoprene nitrate chemistry and grid resolution. J Geophys Res 114:D09301. doi:10.1029/2008JD011254

Lin G, Penner JE, Sillman S, Taraborrelli D, Lelieveld J (2011) Global mechanistic model of SOA formation: effects of different chemical mechanisms. Atmos Chem Phys Discuss 11:26347–26413

O'Connor FM et al (2010) Possible role of wetlands, permafrost, and methane hydrates in the methane cycle under future climate change: a review. Rev Geophys 48:RG4005. doi:10.1029/2010RG000326

Pierce T, Geron C, Bender L, Dennis R, Tonnesen G, Guenther A (1998) Influence of increased isoprene emissions on regional ozone modeling. J Geophys Res 103:25611–25630

Prather MJ (2007) Lifetimes and time scales in atmospheric chemistry. Philos Trans R Soc Math Phys Eng Sci 365:1705–1726

Tarnocai C, Canadell JG, Schuur EAG, Kuhry P, Mazhitova G, Zimov S (2009) Soil organic carbon pools in the northern circumpolar permafrost region. Global Biogeochem Cycles 23:GB2023. doi:10.1029/2008GB003327

Wang JS, Logan JA, McElroy MB, Duncan BN, Megretskaia IA, Yantosca RM (2004) A 3-D model analysis of the slowdown and interannual variability in the methane growth rate from 1988 to 1997. Global Biogeochem Cycles 18:GB3011. doi:10.1029/2003GB002180

West JJ, Fiore AF, Horowitz LW, Mauzerall DL (2006) Mitigating ozone pollution with methane emission controls: global health benefits. Proc Natl Acad Sci 103(11)