OZONE

Ozone is a molecule composed of three oxygen atoms. It is formed throughout the lower part of the Earth's atmosphere through a series of chemical reactions involving sunlight and ozone precursors such as volatile organic compounds (VOCs) and oxides of nitrogen (NO_x). Carbon monoxide (CO) and methane (CH_4) also contribute to ozone formation. These precursors are emitted from a variety of man-made sources including industrial facilities, power plants, landfills, and motor vehicles. Precursor emissions from natural sources such as lightning, soil, and trees also contribute to ozone formation. Ozone at ground level is associated with adverse health and welfare effects, and EPA has set national standards and designed control programs to protect against this "bad" ozone (see Figure 7). Additionally, ozone occurring throughout the tropospheric (lower) region of the Earth's atmosphere acts as a greenhouse gas (GHG), trapping heat from the sun and warming the Earth's surface. Ozone that occurs higher up in the stratospheric region of the atmosphere is generally natural in origin and forms a protective layer that shields life on Earth from the sun's harmful rays. EPA works to protect this "good" ozone in the upper atmosphere through regulations on ozone-depleting substances like chlorofluorocarbons (CFCs).

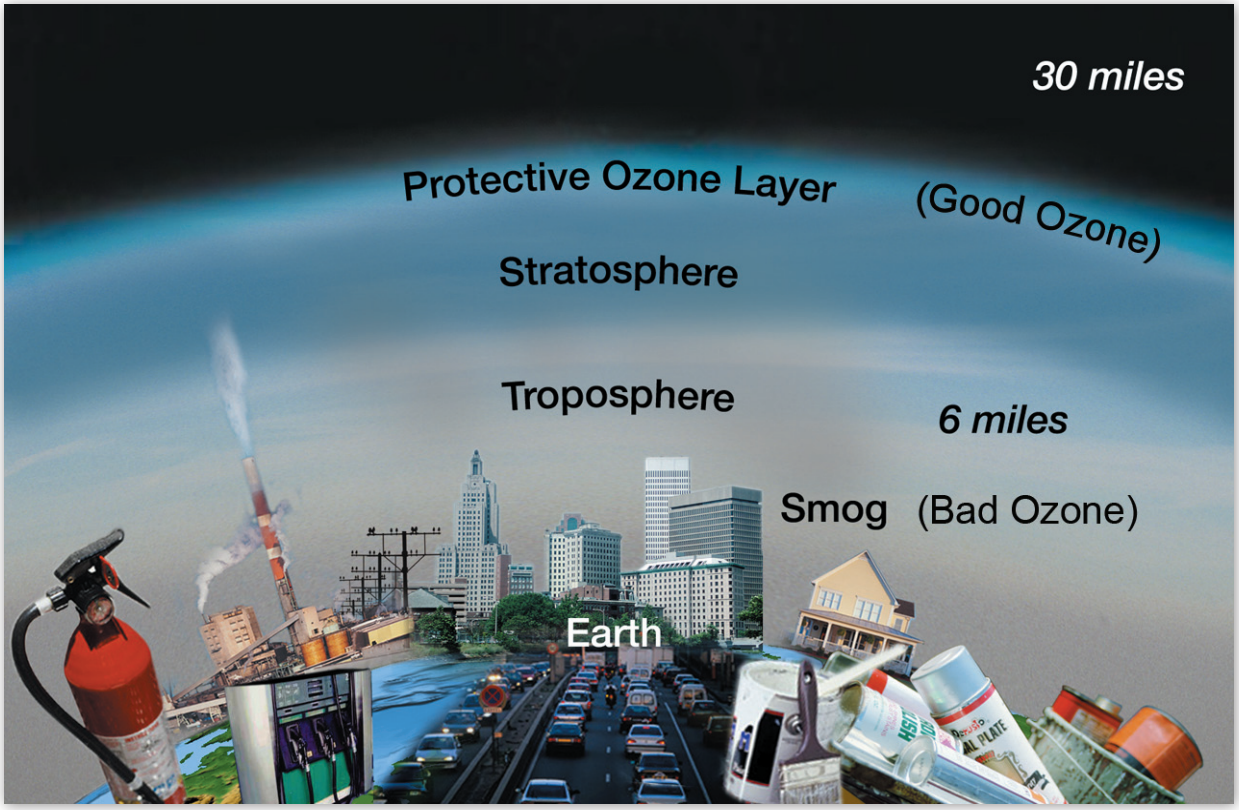


Figure 7. Ozone occurs both in the Earth's upper atmosphere (stratosphere) and at ground level (troposphere). Most of the adverse health and environmental effects of ozone are associated with ozone in the troposphere, while ozone in the stratosphere actually protects the Earth from harmful solar radiation.

TRENDS IN GROUND-LEVEL OZONE CONCENTRATIONS

Nationally, ground-level ozone concentrations were 10 percent lower in 2008 than in 2001, as shown in Figure 8. The trend showed a notable decline after 2002. Though concentrations in 2008 were among the lowest since 2002, many areas measured concentrations above the 2008 national air quality standard for ozone (0.075 ppm). When comparing two three-year periods (2001-2003 and 2006-2008), 97 percent of the sites show a decline or little change in ozone concentrations, as shown in Figure 9. Sites that showed the greatest improvement were in or near the following metropolitan areas: Anderson, IN; Chambersburg, PA; Chicago, IL; Cleveland, OH; Houston, TX; Michigan City, IN; Milwaukee, WI; New York, NY; Racine, WI; Watertown, NY; and parts of Los Angeles, CA. However, other parts of Los Angeles showed a notable increase in ground-level ozone concentrations. Ozone trends can vary locally, as shown by the presence of increases and decreases at nearby sites.

Twenty-three sites showed an increase of greater than 0.005 ppm. Of the 23 sites that showed an increase, 12 sites measured concentrations above the 2008 ozone standard in the 2006-2008 time period.[1] These sites are located in or near the following metropolitan areas: Atlanta, GA; Baton Rouge, LA; Birmingham, AL; Denver, CO; El Centro, CA; Los Angeles, CA; San Diego, CA; and Seattle, WA.

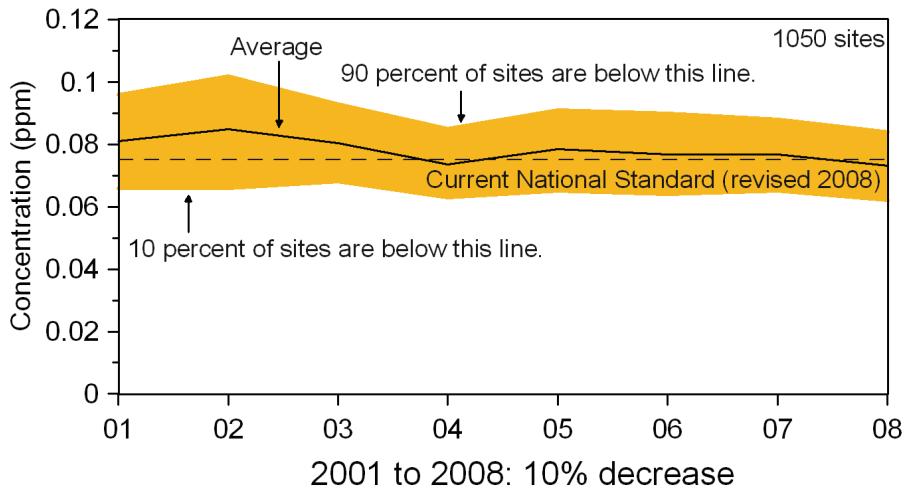


Figure 8. National 8-hour ozone air quality trend, 2001-2008 (average of annual fourth highest daily maximum 8-hour concentrations in ppm).

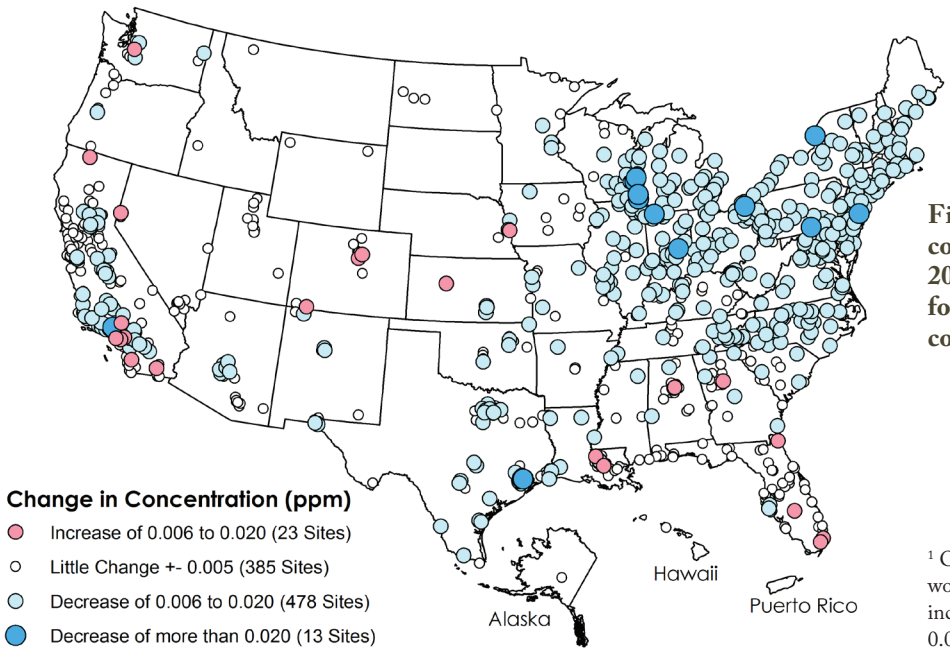


Figure 9. Change in ozone concentrations in ppm, 2001-2003 vs. 2006-2008 (three-year average of annual fourth highest daily maximum 8-hour concentrations).

[1] On September 16, 2009, EPA announced it would reconsider the 2008 ozone NAAQS, which included primary and secondary standards of 0.075 ppm (8-hour average). EPA will propose any revisions to the standards by December 2009 and issue a final decision by August 2010.

Figure 10 shows a snapshot of ozone concentrations in 2008. The highest ozone concentrations were located in California. Note that the high concentration shown in Wyoming occurred at one site due to an unusual combination of local emission and atmospheric conditions on a winter day. Thirty-two percent of all sites were above 0.075 ppm, the level of the 2008 standard.

WEATHER INFLUENCES OZONE

In addition to emissions, weather plays an important role in the formation of ozone. A large number of hot, dry days can lead to higher ozone levels in any given year, even if ozone-forming emissions do not increase. To better evaluate the progress and effectiveness of emissions reduction programs, EPA uses a statistical model to estimate the influence of atypical weather on ozone formation.

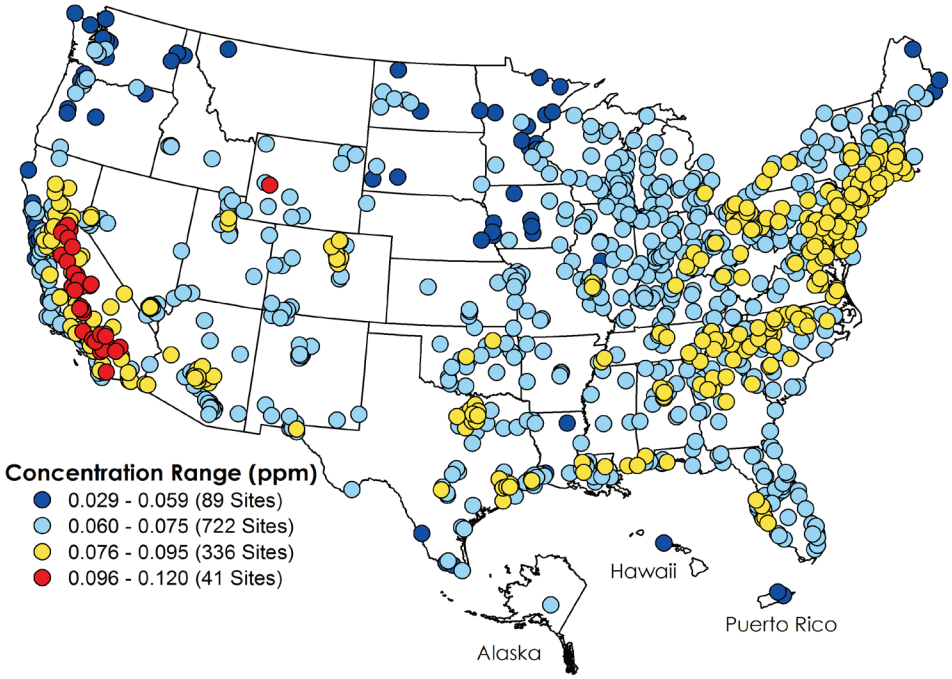


Figure 10. Ozone concentrations in ppm, 2008 (fourth highest daily maximum 8-hour concentration).

Figure 11 shows ozone trends for 2001 through 2008, averaged across selected sites before and after adjusting for weather. Across these selected sites, observed ozone levels show a decrease of approximately eight percent between 2001 and 2008, compared with a larger decrease of approximately 11 percent after removing the influence of weather variations. By examining the data separately for California vs. the eastern U.S., it is clear that the majority of the ozone improvement, after adjusting for weather, occured in the East (on the order of 15 percent).

The largest changes in both observed and weather-adjusted ozone in the East occurred during the period of 2002 to 2004 and was especially noticeable between 2003 and 2004 for the weather-adjusted trend. This relatively abrupt change in ozone levels coincides with the large NO_x emission reductions brought about by implementation of the NO_x SIP Call rule, which began in 2003 and was fully implemented in 2004. This significant improvement in ozone continues into 2008, i.e., weather-adjusted levels in 2008 are the lowest over the eight-year period. In 2007, weather conditions contributed to higher than average ozone formation in the East, as shown by the large difference between adjusted and observed ozone. In contrast, 2008 showed a small difference between adjusted and observed ozone indicating that weather variation had less of an impact on ozone formation.

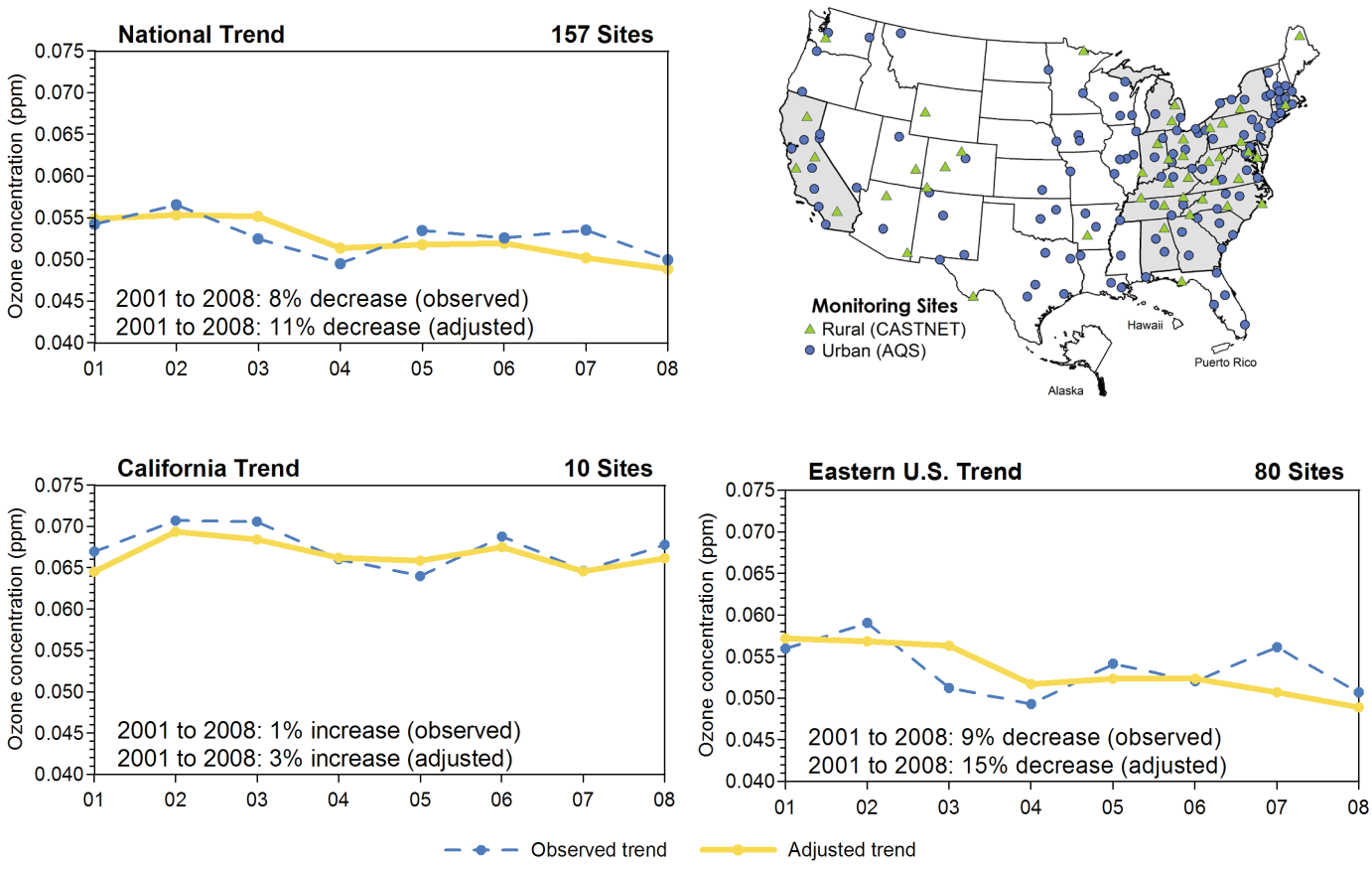


Figure 11. Trends in average summertime daily maximum 8-hour ozone concentrations in ppm (May-September), before and after adjusting for weather nationally, in California, and in eastern states, and the location of rural and urban monitoring sites used in the averages.

Notes: Urban areas are represented by multiple monitoring sites. Rural areas are represented by a single monitoring site. For more information about the Air Quality System (AQS), visit http://www.epa.gov/ttn/airs/airsaqs. For more information about the Clean Air Status and Trends Network (CASTNET), visit http://www.epa.gov/castnet/.

OZONE'S EFFECTS ON CLIMATE

The Intergovernmental Panel on Climate Change (IPCC) indicates that tropospheric ozone is the third most important GHG after carbon dioxide (CO_2) and methane (CH_4) in terms of global average climate forcing, as shown in Figure 12.

At any given location, the local ozone concentrations are the sum of three separate components: (1) ozone produced by local emissions and meteorology, (2) transported ozone produced elsewhere in the region, and (3) ozone transported on hemispheric scales (global background levels of ozone) (Dentener, 2004). The time scales and mechanisms for ozone formation, transport, and destruction vary across these three contributors. Local formation typically occurs on the scale of hours, whereas regional and hemispheric transport can occur over days and weeks, respectively. Traditionally, most efforts to improve ozone air quality have been aimed at reducing the local and regional

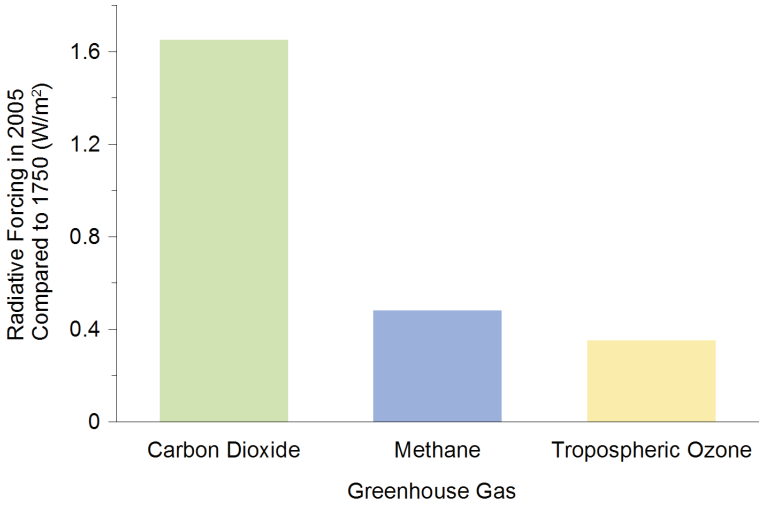
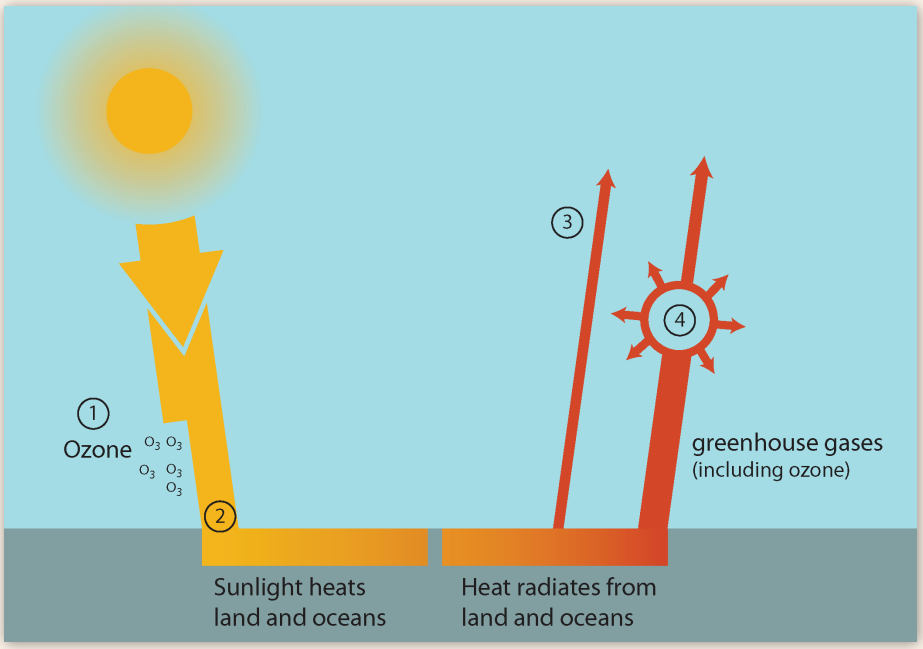


Figure 12. Net radiative forcing (Watts per m²) associated with the three most important GHGs, based on concentrations in 2005 compared to pre-industrial levels. As these GHGs increased, absorption of radiation by these gases and consequent warming of the atmosphere also increased. (Source: National Academy of Sciences, 2005)

UNDERSTANDING THE CONTRIBUTION OF TROPOSPHERIC OZONE TO CLIMATE CHANGE



(1) Sunlight absorbed by ozone warms the air.
(2) Sunlight absorbed by land and oceans warms the Earth's surface.
(3) Energy radiates from land and oceans to space.
(4) Most energy radiated from land and oceans is absorbed by greenhouse gases, including ozone, which warm the air and re-radiate energy in all directions.

As solar energy passes through the Earth's atmosphere, some of it is absorbed or scattered by water vapor, aerosols, clouds, and gases like ozone. Tropospheric ozone warms the atmosphere partly by absorbing this direct and reflected energy from the sun (yellow in figure). Most of the atmospheric warming from tropospheric ozone comes from absorption of infrared energy radiated back toward space from the Earth's surface. The tendency for ozone to absorb reflected energy and "trap" heat is especially significant over surfaces such as ice and snow, which normally reflect a large percentage of incoming solar radiation back to space.

Radiative forcing: The change in the energy balance between incoming solar radiation and exiting infrared radiation, typically measured in watts per square meter (W/m^2). Positive radiative forcing tends to warm the surface of the Earth while negative forcing generally leads to cooling.

contributions via controls of local VOC emissions and local/regional NO_x emissions. These efforts have resulted in significant improvements in ground-level ozone concentrations over the U.S. in recent years. It should be noted that global background levels of ozone are very important for climate considerations because ozone formed from emissions in U.S. urban areas and regions represents only a fraction of the overall global ozone and its resulting impacts on warming. Global ozone background levels are determined by global emissions of CH_4, CO, NO_x, and VOCs, as well as natural processes like lightning and transport from the stratosphere. Numerous field studies have shown that these global background ozone concentrations can approach 40 ppb (Jacob, 2007) and have been increasing in recent years (Parrish, 2009).

CONTROL STRATEGIES

Current U.S. ozone reduction strategies have tended to focus on reducing peak concentrations rather than background levels and have also focused more on NO_x reductions than on reductions of other ozone precursors in most locations. While such strategies have been successful in reducing ground-level ozone concentrations for the purpose of meeting the National Ambient Air Quality Standards (NAAQS) and protecting public health, it may be necessary to re-evaluate these control programs for their impact on climate.

Reducing the emissions of ozone precursors will generally decrease ozone production and cool the atmosphere. In some cases, however, reducing one precursor by itself may not be sufficient. Reductions in NO_x alone, for example, increase the lifetime of CH_4, which has a warming influence on the atmosphere. To be most beneficial for climate and air quality, ozone reduction strategies involving NO_x should also target reductions in CH_4, VOCs, and/or CO, which contribute substantially to global background levels of ozone (Quinn, 2008).