12.1 Tropospheric Ozone

12.1.1 General Information

Ozone is ubiquitous throughout the troposphere; the concentration is highest in urban areas, but it is also present in remote areas. The global distribution is due to atmospheric transport processes (winds, mixing, convection) as well as the presence of its chemical precursors, NO_x and VOCs.

12.1.2 Sources and Sinks

Figure 12-3 shows the tropospheric sources and sinks for ozone. There are two sources for tropospheric ozone – 1) transport from the stratosphere (400 Tg/year) and 2) photo-chemical reactions involving NO_x and reactive carbon (CO, CH_4, and NMVOC) in the presence of sunlight (4,300 Tg/year). Ozone has no significant anthropogenic emission sources, although it is useful as a water treatment disinfectant. The sinks for ozone include 1) photochemical degradation and reaction with water to form hydroxyl radicals (4,000 Tg/year) and deposition on the earth's surface (700 Tg/year). Note that 1 Tg $= 10^{12}$ grams.

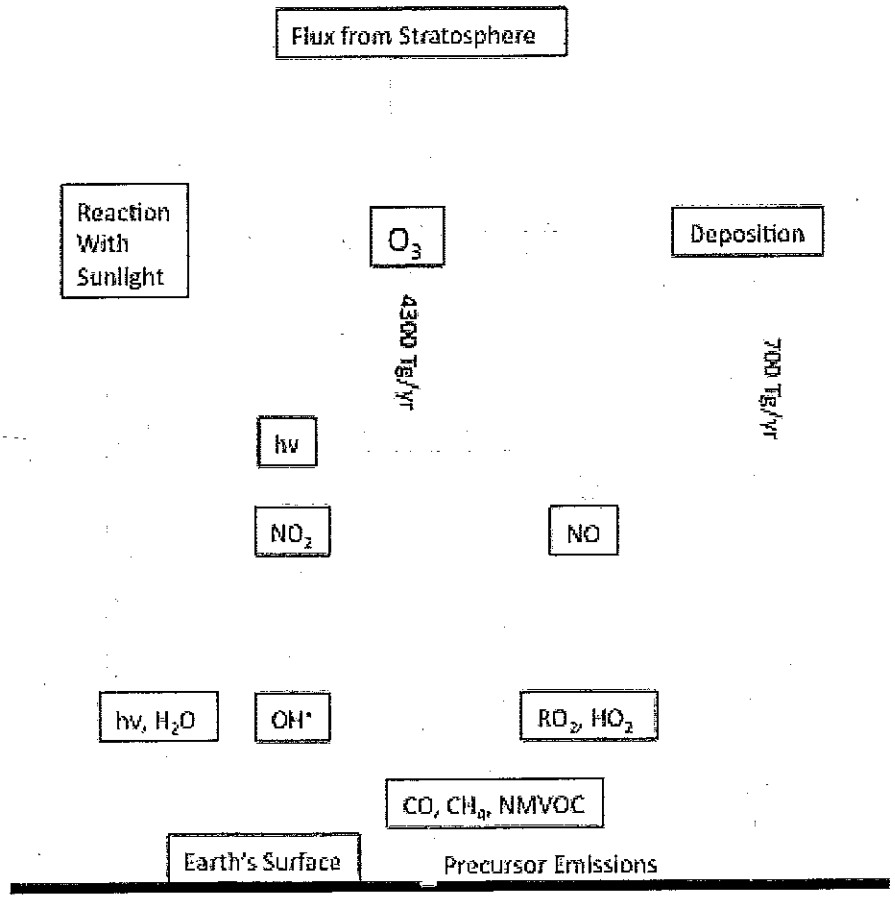


FIGURE 12-3. Sources and Sinks of Ozone (O_3) in the Troposphere. Number values represent ozone flux in Teragrams (10^{12} g) per year.

Ozone is generated in the stratosphere through the interaction of oxygen and sunlight (see section 12.2). Normally, there is little mixing between the stratosphere and troposphere. However, there are certain conditions that can lead to stratospheric air being pulled into the troposphere and then mixing. This weather phenomenon is called *tropopause folding*. It occurs when a large cold front passes beneath a jet stream (large river of air moving much faster than the air around it), which causes a downward motion of the tropopause and the stratosphere on the windward (upwind) side of the jet-stream. The mixed region is large: 100 - 200 km long, 100 – 300 km wide, and 1 – 4 km thick. It typically only brings air from the stratosphere to the upper and middle regions of the troposphere. It is rare for this air mass to be transported directly to ground level. Once in the troposphere, the ozone (and other constituents) can migrate to ground level by diffusion and convection. This mechanism accounts for 40 – 60% of the background level of ozone in the troposphere. Prior to studies in the 1960's and 1970's, this was believed to be the only source of ozone in the troposphere.

The other source of O_3 in the troposphere is due to chemical reactions between ozone precursors: nitrogen oxides (NO_x), reactive carbon (CO, CH_4, and NMVOC), and sunlight. These reactions are why ozone is a secondary air pollutant. Secondary means not directly emitted but generated from other pollutants. The formation of O_3 and other oxidants and oxidation products from these precursors is a complicated and nonlinear relationship between many factors: the concentrations and ratios of the precursors in ambient air; the intensity and spectral distribution of sunlight; atmospheric mixing; temperature; presence of catalytic particles; and the rates of chemical reactions between ozone and its many precursors. These processes can also lead to the formation of other photochemical products, such as peroxyacetyl nitrate (PAN), nitric acid (HNO_3), sulfuric acid (H_2SO_4), formaldehyde (CH_2O), and other carbonyl compounds, such as aldehydes and ketones.

The most important variables are the concentrations of NO_x and VOC, and the VOC/NO_x ratio. NO_x concentrations are highest in urban areas due to emissions from automobiles and fossil fuel combustion. VOCs have many natural and human sources. VOC concentrations in urban areas are usually high due to the use of fossil fuels, but may also be high near forested areas (see Chapter 11).

Regions with low NO_x concentrations, such as rural, suburban, and remote continental areas have an increase in O_3 production with increasing NO_x. At higher concentrations found in urban areas, especially near busy streets and highways and in power plant plumes, there is a decrease in O_3 production due to the reaction with NO. In between these two regimes, O_3 production shows only a weak dependence on NO_x concentrations. The rate of O_3 production per NO_x oxidized is highest in areas where NO_x concentrations are lowest and decreases with increasing NO_x concentration. In regions with low VOC concentrations, the NO_x competes with VOC for available hydroxyl radicals, decreasing the rate of VOC oxidation and subsequently the rate of ozone production.

Classes of organic compounds important for the photochemical formation of O_3 include alkanes, alkenes, aromatic hydrocarbons, carbonyl compounds, alcohols, organic peroxides, halogenated organic compounds, and carbon monoxide. These compounds have a wide range of chemical properties and lifetimes: the atmospheric lifetime of isoprene is about one hour, and methane

is about a decade. In urban areas, all classes of reactive carbon are important for O_3 formation. In nonurban vegetated areas, biogenic VOCs emitted from vegetation (isoprene and monoterpenes) tend to be the most important. In the upper and middle troposphere, CH_4 and CO are the main carbon-containing precursors to O_3 formation.

The photochemical formation of O_3 results from the photolysis of nitrogen dioxide (NO_2) to nitric oxide (NO) and a ground-state oxygen atom, (O). This free oxygen then reacts with molecular oxygen in the presence of a catalyst (M) to form O_3:

12.1 $NO_2 + h\nu \rightarrow NO + O$ for $\lambda < 430nm$

12.2 $O + O_2 + M \rightarrow O_3 + M$

12.3 $NO + O_3 \rightarrow NO_2 + O_2$

Where: O is a free oxygen atom in its ground state
$h\nu$ = energy from an absorbed photon (J)
Where h = Planck's constant (6.63×10^{-34} J s)
ν= frequency of photon (= c/λ, where c = 3×10^8 m/s)
λ = wavelength of the photon (measured in nm)

The reaction of NO to NO_2 is enhanced by the availability of organic (RO_2) or hydroperoxy (HO_2) radicals, see equations 12.6 and 12.18. These radicals form during the oxidation of reactive carbon. When reaction 12.3 occurs, it leads to additional NO_2, which increases the formation of ozone by the above equations (12.1 and 12.2). The presence of reactive carbon enhances the formation of ozone from the photolysis of NO_2. However, without NO_x, these compounds would not produce ozone.

The following sets of reactions provide one possible reaction scheme for the oxidation of reactive carbon in the presence of NO_x leading to the formation of ozone. Note that RH represents a VOC, where R is the carbon chain, and H represents one hydrogen atom bound to the molecule, R' is an organic fragment having one less carbon than R, M is a third body that transfers energy to/ from the reaction, the dot superscript denotes that the molecule is in its radical form (missing an electron), and $h\nu$ represents a unit of energy from a photon (see equation 12.1) typically provided by sunlight:

12.4 $RH + OH\cdot \rightarrow R\cdot + H_2O$

12.5 $R\cdot + O_2 + M \rightarrow RO_2\cdot + M$

12.6 $RO_2\cdot + NO \rightarrow RO\cdot + NO_2$

12.7 $RO\cdot + O_2 \rightarrow HO_2\cdot + R'CHO$

12.8 $HO_2\cdot + NO \rightarrow OH\cdot + NO_2$

12.1 $2\,[NO_2 + h\nu \rightarrow NO + O]$

12.2 $2\,[O + O_2 + M \rightarrow O_3 + M]$

Overall:

12.9 $RH + 4\,O_2 + 2\,h\nu \rightarrow R'CHO + H_2O + 2\,O_3$

Oxidation of methane dominates ozone production in air where the NMVOC concentrations are small:

12.10 $CH_4 + OH\cdot + \rightarrow CH_3\cdot + H_2O$

12.11 $CH_3\cdot + O_2 + M \rightarrow CH_3O_2\cdot + M$

12.12 $CH_3O_2\cdot + NO \rightarrow CH_3O\cdot + NO_2$

12.13 $CH_3O\cdot + O_2 \rightarrow HO_2\cdot + CH_2O$

12.14 $HO_2\cdot + NO \rightarrow OH\cdot + NO_2$

12.1 $2\,[NO_2 + h\nu \rightarrow NO + O]$

12.2 $2\,[O + O_2 + M \rightarrow O_3 + M]$

Overall:

12.15 $CH_4 + 4\,O_2 + h\nu \rightarrow CH_2O + H_2O + 2\,O_3$

A similar mechanism for carbon monoxide:

12.16 $CO + OH\cdot \rightarrow CO_2 + H\cdot$

12.17 $H\cdot + O_2 + M \rightarrow HO_2\cdot + M$

12.18 $HO_2\cdot + NO \rightarrow OH\cdot + NO_2$

12.1 $NO_2 + h\nu \rightarrow NO + O$

12.2 $O + O_2 + M \rightarrow O_3 + M$

Overall:

12.19 $CO + 2\,O_2 + h\nu \rightarrow CO_2 + O_3$

Note that oxidation products from methane and NMVOC are themselves further oxidized until they form carbon dioxide and water.

The main sinks for ozone include deposition onto the earth's surface and photochemical reaction with water to form hydroxide and molecular oxygen. Surface deposition occurs when the ozone reacts with any oxidizable material, and it is greatest above growing vegetation. The photochemical loss is due to the following reactions:

12.20 $O_3 + h\nu \rightarrow O_2 + O\cdot$

12.21 $O\cdot + H_2O \rightarrow 2\,OH\cdot$

12.22 $HO_2\cdot + O_3 \rightarrow OH\cdot + 2\,O_2$

While this mechanism suggests a route of photochemical loss of tropospheric ozone, it generates a significant amount of OH radical. Recall that the hydroxyl radical (OH) plays a significant role in the photochemical oxidation of hydrocarbons and the formation of ozone. It is not clear that this reaction leads to a net loss in ozone.

The photochemical lifetime of ozone in the troposphere depends on the season, latitude and elevation of a location. Lifetimes range from a few days to a few weeks in the summer, whereas it can be three months in the winter. Table 12-1 shows a model calculated photochemical lifetime of O_3 at various altitudes, seasons, and latitudes (Brasseur, et al., 1999).

Table 12-1. Photochemical Lifetime (days) of Ozone in the Troposphere.

Latitude →	40 °N		20 °N	
Altitude (km)	Summer	Winter	Summer	Winter
0	8	100	5	17
5	15	160	10	35
10	40	300	30	90

The ambient concentration of ozone depends on the time of day, season, temperature, and location. The reactions creating tropospheric ozone depend on the availability of sunlight as well as the

chemical precursors. Ambient O_3 concentrations are higher during warmer seasons and during the weekday, peaking during the later portion of the day.

12.1.2.1 Daily Variations

Ozone concentrations vary over the course of a day. Ozone formation depends on the interaction between solar energy and its chemical precursors. At night, ozone concentration declines due to its participation in oxidation reactions and lack of sunlight. The maximum rate of formation coincides with maximum solar radiation – typically occurring between 10 am and 2 pm. The maximum concentration usually lags this time because the rate of formation is greater than the rate of its destruction. Ozone concentrations tend to peak early- to mid-afternoon in areas where there is strong photochemical activity and later in the day in areas where transport from upwind regions is the main source. Also, nighttime automobile emissions of NO in urban areas can reduce O_3 to low levels overnight.

12.1.2.2 Seasonal Variations

Ozone is typically a summertime pollutant. Summer is the time when the most sunlight is available; temperatures are higher, and the largest emissions of natural sources of VOCs occur. Monthly maxima can occur any time from June through August. However, springtime maxima are observed in national parks, mainly in the western United States and at a number of other relatively unpolluted monitoring sites throughout the Northern Hemisphere. For example, the highest O_3 concentrations at Yellowstone National Park (Wyoming, Montana, and Idaho, USA) tend to occur during April and May. Monthly minima O_3 concentrations tend to occur from November through February at polluted sites and during the fall at relatively remote sites. The springtime peaks may be the result of stratospheric ozone intrusion events (see tropopause folding, section 12.1.2).

12.1.2.3 Temperature Dependency

The reactions that generate ozone are temperature dependent; as temperature rises, so do the rates of reaction. The photochemical process responsible for the formation of tropospheric ozone typically becomes important when the ambient temperature exceeds 15°C (Alley, et al., 1962).This means that, in the mid-latitudes, ozone is rarely a concern during winter months. Many regions do not require testing or collecting data for ozone during the winter months. However, high concentrations of wintertime ozone can occur in valleys. These occur because snow cover enhances solar insolation (through reflection) into a shallow boundary layer where local VOC and NO_x emissions are trapped.

12.1.2.4 Location Dependency

In western North America, the presence of mountain barriers limits atmospheric mixing (as in Los Angeles, Salt Lake City, and Mexico City) and causes a higher frequency and duration of days with high O_3 concentrations. In eastern North America, high O_3 concentrations are associated with summer weather and high-pressure weather systems. Such events can extend over hundreds of thousands of square kilometers for several days. Ozone concentrations in southern urban areas (such as Houston, TX and Atlanta, GA) tend to decrease with increasing wind speed. In northern cities (such as Chicago, IL; New York, NY; Boston, MA; and Portland, ME), the average O_3 concentrations over metropolitan areas increase with wind speed, indicating that transport of O_3 and its precursors from upwind areas is important [(Husar, et al., 1998); (Schichtel, et al., 2001)]. Ozone in city centers tends to be lower than in regions either upwind or downwind because of destruction by NO emitted by motor vehicles, see equation 12.28.

An additional location dependency is associated with precursor pollutant sources – the eastern US has a higher population density, and greater automobile emissions than the western US. Also, there is a general west to east direction of surface winds. Other cities, such as Houston, TX, have large sources of VOCs from local petroleum based industries. In general, the eastern US has regional (multiple state) ozone problems and the western US ozone problems are more confined to urban areas.

12.1.3 Health and Welfare

12.1.3.1 Effect on Human Health

Numerous scientific studies have linked ground-level ozone exposure to a variety of problems, including:

- Shortness of breath;
- Wheezing and breathing difficulties during exercise or outdoor activities;
- Coughing and sore or scratchy throat;
- Pain when taking a deep breath;
- Increase the frequency of asthma attacks;
- Aggravate and increase susceptibility to respiratory illnesses like pneumonia, asthma, emphysema, and bronchitis;
- Inflame and damage the lung lining;
- Reduce lung function; and
- Permanent lung damage with repeated exposures.

These effects may lead to increased work and school absences, visits to doctors and emergency rooms, and hospital admissions. Research also indicates that ozone exposure may increase the risk

of premature death from heart or lung disease. A recent report suggests that 4 to 6% of heart attacks in the US can be linked to air pollution (Brook, et al., 2004). These affects begin to appear in healthy populations at air concentrations between 40 - 80 ppbv of ozone [(Adams, 2002), (Adams, 2003), (Adams, 2006)]. The symptoms become stronger and affect larger percentages of the population as the concentration increases. The OSHA exposure limit is 100 ppbv time weighted average for a 10 hour workday during a 40 hour workweek. The IDLH (immediately dangerous to life or health) level is 5,000 ppbv (NIOSH, 2011).

Some people are more sensitive to ozone than others. Sensitive groups include - children; healthy adults who are active outdoors; people with lung disease, such as asthma, emphysema, or chronic bronchitis; and older adults. Direct evidence of human health effects due to O_3 exposure are obtained through controlled human exposure studies of volunteers or field and epidemiologic studies of populations exposed to ambient O_3. Controlled human exposure studies typically use fixed concentrations of O_3 under carefully regulated environmental conditions and subject activity levels. The majority of controlled human studies have investigated the effects of exposure to O_3 in young nonsmoking healthy adults (18 to 35 years of age) performing continuous exercise (CE) or intermittent exercise (IE). These studies use various combinations of O_3 concentration, exercise routine, and exposure duration. The most salient observations from studies the US-EPA reviewed were that: young healthy adults exposed to O_3 concentrations of 60 ppbv develop significant reversible, harmful effects (as listed above), and higher concentrations increased the negative effects [(US-EPA, 1996), (US-EPA, 2006a).

It is interesting to note that some of the early 20th century measurements of ground level atmospheric ozone were done at European alpine sites (e.g., Arosa, Switzerland) because people were encouraged to visit these sites to take the ozone rich air for their health.

12.1.3.2 Effect on Human Welfare

Ground-level ozone can have detrimental effects on plants and ecosystems. These effects include:

- interference with the ability of sensitive plants to produce and store energy,
- increased susceptibility to diseases, insects, other pollutants, and weather;
- damage to the leaves of trees and other plants negatively impacting their appearance; and
- reduced forest growth and crop yields.

Sensitive plant species that are potentially at increased risk from ozone exposure include trees such as black cherry, quaking aspen, ponderosa pine, and cottonwood. These trees are found across the United States, including in protected parks and wilderness areas. Not all species are equally sensitive to ozone.

(Murphy, et al., 1999) estimated the yearly damage from motor vehicle ozone precursor emissions (NO_x and VOCs) caused losses of $2.8 billion to $5.8 billion (1990 dollars) to the eight largest production crops. The US-EPA estimates the loss in crop production due to just ozone at $500

million each year (US-EPA, 2010a). Air pollutant effects on tree species and forest habitats have resulted in measurable changes in total biomass, changes in composition of forest species (biodiversity), and forest health [(Kurczynska, et al., 1997), (Bringmark, et al., 1995), (McLaughlin, et al., 1999), (Vacek, et al., 1999)]. No loss estimate is available for changes in forest biomass and composition because this is more difficult to quantify than marketable products, and there is little agreement in how to value these natural services.

Ozone and other photochemical oxidants also react with many economically important man-made materials, decreasing their useful life and aesthetic appearance. Some susceptible materials include elastomers, fibers, dyes, and paints [Chapter 11 from (US-EPA, 2006a)].

Elastomers such as natural rubber, synthetic butadiene, isoprene, and styrene polymers and copolymers are particularly susceptible to even low concentrations of O_3. Ozone damages these compounds by breaking the molecular chain at carbon double bonds; a chain of three oxygen atoms is added directly across the double bond. The change in structure promotes the characteristic cracking of stressed/ stretched rubber called "weathering." Tensile strain produces cracks on the surface of the rubber that increase in number with increased strain. The rate of crack growth is dependent on the degree of stress, the type of rubber compound, O_3 concentration, time of exposure, and temperature. After initial cracking, there is further O_3 penetration, resulting in additional cracking, loss of strength, decrease in ductility and eventually failure. One of the first tests for ozone was to stretch a rubber band around a jar and see how long it took to break (AQMD, 1997). High levels of ozone could cause the rubber band to snap in less than 15 minutes.

Ozone can damage textiles and fabrics by methods similar to those associated with elastomers. Synthetic fibers are less affected by O_3 than natural fibers; however, O_3 contribution to the degradation of textiles and fabrics is not very significant, resulting only in slight decreases in fiber strength.

Ozone causes color fading in textile dyes by reacting with the dye molecules. Ozone molecules break the aromatic ring portion of the dye molecule, oxidizing the dye. The rate of fading depends upon the rate of diffusion of the dye to the fiber surface. The type of textile fiber and the manner of dye application influence the rate and severity of the O_3 attack. Several artists' pigments are also sensitive to fading and oxidation by O_3 when exposed to concentrations found in urban areas. Because of the potential of O_3 to damage works of art, recommended limits on O_3 concentrations in museums, libraries, and archives are relatively low, ranging from 10 to 15 ppbv. These facilities use air de-ozonators as part of their air conditioning systems when outside air exceeds these concentrations.

Ozone acts to erode some surface coatings (paints, varnishes, and lacquers). However, many of the available studies on O_3 degradation of surface coatings do not separate the effects of O_3 from those of other pollutants or environmental factors such as weather, humidity, and temperature. In addition, many manufacturers alter the materials or add additional components to reduce the harmful effects of environmental factors.

12.1.4 History and Regulation

Table 12-2 shows the O_3 ambient air quality standard for several countries. The values are based on statistical evidence from epidemiological studies and short-term chamber experiments.

Table 12-2. Ozone Ambient Air Quality Standards in Several Countries.

Country / Time Period Average Units (unless noted)	8-hr $\mu g/m^3$	1-hr $\mu g/m^3$
US	150	
EU	120	
Japan		120[A]
India (Class I/II/III)	100/100/100	180/180/180
China (Class I/II/III)		120/160/200
Brazil		160
Mexico	150[A]	
South Africa		235
WHO	100	

Notes:
Class I: Tourist, conservation; Class II: Residential; Class III: Industrial and Heavy Traffic.
A - Includes all photochemical oxidants (e.g. O_3, PAN)

The US-EPA establishes National Ambient Air Quality Standards (NAAQS) for ground-level ozone (O_3) and other criteria pollutants based on human health and welfare standards. The 1970 Clean Air Act (CAA) and the 1990 Clean Air Act Amendments (CAAA) authorized the process for determining and implementing these standards. Table 12-3 provides a brief timeline of the milestones in the development and implementation of ambient air ozone standards in the US (US-EPA, 2010b).

Under the CAA and CAAA each state must develop a plan describing how it will attain and maintain the NAAQS. The plan is called the State Implementation Plan (SIP). A SIP is a collection of programs (e.g. monitoring, modeling, emission inventories, control strategies) and documents (policies, rules, and enforcements) that the state uses to attain and maintain the NAAQS for all air contaminants, see section 3.2. A state must engage the public in approving its plan prior to sending it to EPA for approval. In some cases where the EPA fails to approve a SIP, the Agency can issue and enforce a Federal Implementation Plan (FIP) to ensure attainment and maintenance of the NAAQS. The SIP is a working document revised as often as needed.

Table 12-3. History of US-EPA Ground-level Ozone Standards.

Year	Action
1971	EPA established a 1-hour NAAQS ozone standard of 0.08 ppm.
1979	EPA revised the 1-hour standard to 0.12 ppm.
1991	The number of counties designated for non-attainment reached 371. Concerned about the new science indicating adverse effects at levels allowed by the NAAQS, the American Lung Association went to court to compel EPA to act.
1994	EPA obtained a voluntary remand based on a promise to consider the newer studies.
1995	EPA and 37 eastern states form the Ozone Transport Assessment Group - work with stakeholders to study ozone transport for two years.
1996	EPA issued a three-volume criteria document encompassing hundreds of new scientific studies, finding "strong" scientific evidence of adverse health effects from ozone at levels allowed by the 1979 NAAQS (US-EPA, 1996).
1997	(July) EPA revised the air quality standards for ozone replacing the 1979 standard with an 8-hour standard set at 0.08 ppm. Three states and dozens of industry plaintiffs quickly challenged the new standards. (October) EPA acts on the work of the Ozone Transport Assessment Group and proposes NO_x regional reductions in the eastern US.
1998	EPA issued a final rule on regional NO_x reductions, known as the NO_x SIP Call (see chapter 10).
1999	The DC Circuit Court of Appeals sent the 1997 standards back to EPA for further study. EPA appealed.
2001	The U.S. Supreme Court unanimously upheld the constitutionality of the Clean Air Act as EPA had interpreted it in setting the 1997 health-protective air quality standards. ***The Supreme Court also reaffirmed EPA's long-standing interpretation that it must set these standards based solely on public health considerations without consideration of costs.***
2002	EPA began the process by which states (governors) and tribes submit recommendations for what areas would be designated non-attainment (failing to meet the 1997 standard).
2003	(June) EPA proposed the clean air ozone implementation rule with options for how areas would transition from the 1-hour ozone standard to the 8-hour ozone standard. (July) States and tribes recommended designations - 412 counties included. (December) EPA responded to states and tribes describing intended modifications to their recommended designations - 506 counties included. (December) EPA proposed the Clean Air Interstate Rule (CAIR) to help areas in the US meet the 8-hour ozone standard.
2004	EPA finalized the Clean Air Ozone designations and basic implementation rule.
2008	EPA reduced the National Ambient Air Quality Standards for ground-level ozone, from 0.08 ppmv to 0.075 ppmv.

2010	EPA announces plans to reconsider its 2008 decision setting national standards for ground-level ozone – the 2008 level conflicted with the CASAC report showing adverse effects at lower concentrations. The 2009 Clean Air Interstate Rule (CAIR), which is currently in effect, set the values lower. However, CAIR has been vacated by the courts, and EPA has been ordered to address flaws in the law, while leaving CAIR in place temporarily. The first revision, the Cross-State Air Pollution Rule, was stayed in August 2012, and CAIR remains in place. The stay was appealed to the Supreme Court by the US Government on December 10, 2013.
2014	U.S. Supreme Court granted the Environmental Protection Agency's (EPA) motion to lift the stay of the Cross-State Air Pollution Rule (CSAPR). EPA begins implementation of CSAPR.

The CAA requires the US-EPA to review the latest scientific information and standards every five years for each criteria pollutant. New standards and policy decisions undergo review by the scientific community, industry, public interest groups, the general public, and the Clean Air Scientific Advisory Committee (CASAC) before becoming established. Table 12-2 lists the current US primary standard. The secondary (human welfare based) standard is the same as the primary standard. The O_3 concentration is calculated and reported from the 3-year average of the fourth-highest daily maximum 8-hour average ozone concentrations measured at each monitor within an area over each year. If this level does not exceed 0.075 ppm (as of May 27, 2008), the area is designated as in 'attainment.' If the average concentration exceeds this value, the area becomes a 'nonattainment' area. Once 'nonattainment' designations take effect, the state and local governments have three years to develop implementation plans outlining how the area will attain the ambient air standard and how it will maintain the standard. Typical plans include reducing the emissions contributing to ground-level ozone concentrations. The actual methods to bring this about are allowed to vary to the specific circumstances of the area. Most plans include regulations to control stationary sources of NO_x and VOCs. Some include reductions on mobile sources or the fuels used in mobile sources.

The US-EPA has created a set of national and regional rules to reduce emissions of pollutants that form ground-level ozone. The rules affect two main emission sources that release the ozone precursor chemicals (NO_x and VOCs) – stationary fossil-fuel powered sources (power plants) and mobile sources (cars, trucks, planes, ships, and trains). The rules for stationary sources include:

- Clean Air Interstate Rule (2005 and 2009) designed to reduce ground-level ozone in the east by permanently capping emissions of SO_2 and NO_x.
- Clean Air Visibility Rule (2005) amended EPA's 1999 Regional Haze Rule to require emission controls for industrial facilities emitting air pollutants that reduce visibility.
- Regional Transport Rule (1998) reduces regional emissions of NO_x in 22 eastern states (and DC) in order to reduce the regional transport of ozone.

- NO_x SIP Call (1998) reduces the regional transport of NO_x in the eastern US, see chapter10.
- Acid Rain Program (1990) uses a combination of traditional requirements and a market-based cap and trade program to reduce power plant emissions of NO_x and SO_2, see Chapter 9.

The rules for mobile sources include (see Chapter 15 for more detailed information):

- Clean Air Non-Road Diesel Rule (2004) set emission standards for the engines used in construction, agricultural, and industrial equipment, and reduced the amount of sulfur allowed in the fuel they use.
- Clean Diesel Trucks and Buses Rule (2007) issued in December 2000, requires a 95% reduction in emissions of heavy-duty trucks and buses – comparable to achievements made for automobiles.
- Tier 2 Vehicle Emission Standards and Gasoline Sulfur Program, sets tailpipe emissions standards for all passenger vehicles, including SUVs, pickups, vans, and large personal passenger vehicles beginning with the 2004 model year to the same national emission standards as cars. It also requires reduced levels of sulfur in gasoline.
- Emissions standards for highway motorcycles (2005) sets limits on hydrocarbon (HC) and carbon monoxide (CO) emissions for motorcycles based on engine size, see Table 12 4.
- Emission standards for engines (2010) that power forklifts, electric generators, recreational boat engines, snowmobiles, all-terrain vehicles and off-road motorbikes to reduce HC, CO, and NO_x emissions between 35 – 95% depending on engine type (US-EPA, 2001), (US-EPA, 2011a).
- Emission standards for locomotives and marine diesel engines (2004) to reduce sulfur in fuel by 99% and reduce PM and NO_x emissions by as much as 90% and 80% respectively (US-EPA, 2011b), (US-EPA, 2011c).

Table 12-4. US Motorcycle Emission Standards.

Class	Model Year	Emission Standard (g/km) HC	CO
I	2006 and later	1	12
II	2006 and later	1	12
III	2006 - 2009	1.4	12
III	2010 and later	0.8	12

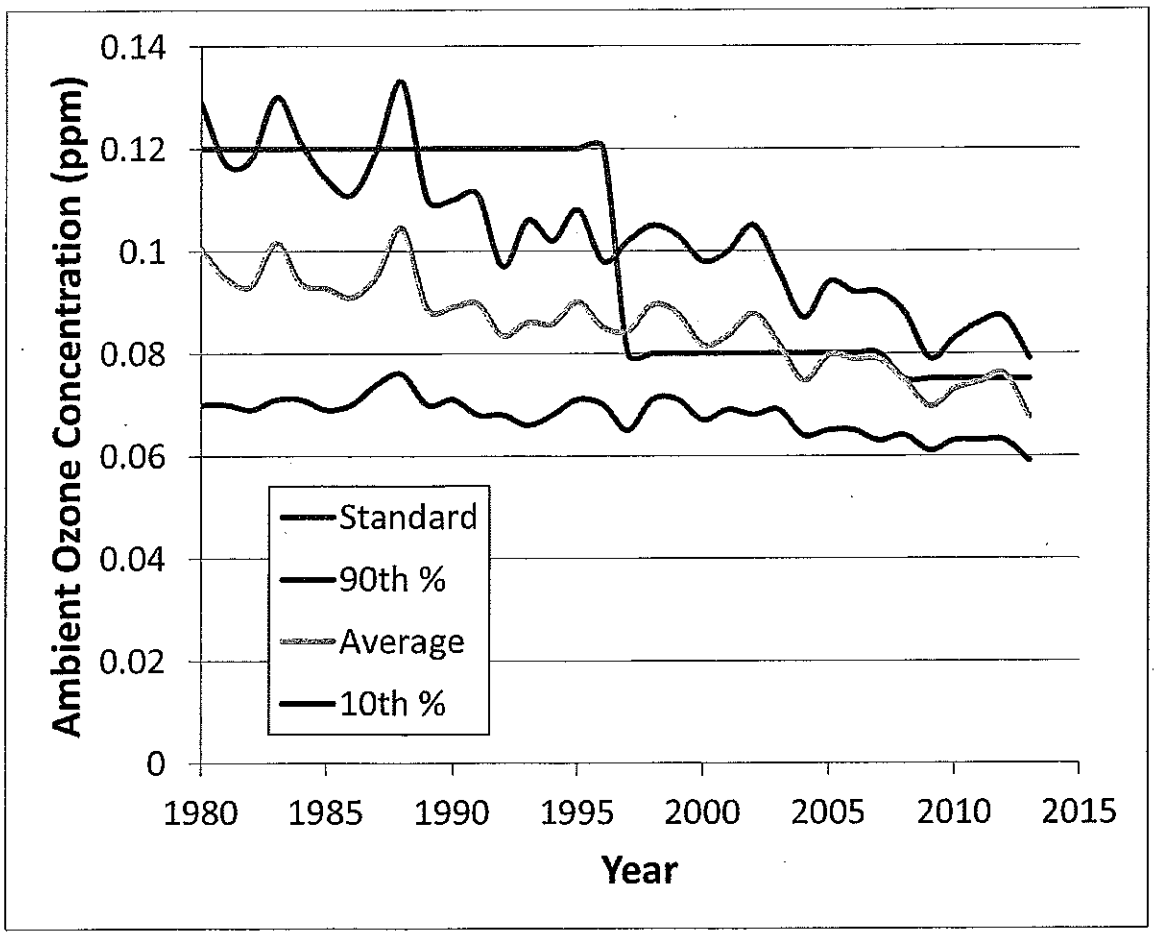
Notes: Class I - Engine Size of 50 to 169 cc (3.1 to 10.4 cu. in.).
Class II - Engine Size of 170 to 279 cc (10.4 to 17.1 cu. in.).
Class III - Engine Size of 280 cc and over (17.1 cu. in. and over).

This list describes the regulatory requirements of manufacturers. Only a few areas in the US require users to have their equipment tested and repaired if necessary. Additional tests may be necessary for areas in ozone non-attainment– that is they have trouble meeting the NAAQS standards.

The US-EPA has also created voluntary programs to help reduce ground-level ozone formation. These programs include the National Clean Diesel Campaign, Voluntary Diesel Retrofit Program, the SmartWay Transport Partnership, and Clean School Buses USA. These programs provide scientific and engineering technical assistance to help states, local governments, and public and private concerns.

Nationwide, the average daily maximum 8-hr O_3 concentrations decreased about 30% from 1980 to 2010, see Figure 12-4. The decrease is larger at the higher end (90th percentile) than at the lower end (10th percentile). The difference in distribution of concentrations is becoming narrower and that the worst locations have improved the most over time. The change is probably due to reductions of NO_x ozone precursors in the most impacted areas, but less in other areas. A look at the trends for NO_2 concentrations (Figure 10-5) shows a similar trend. Most of the US is NO_x limited for ozone formation, hence reductions in NO_x have the most impact.

FIGURE 12-4. US National Air Quality Trend for Ambient O_3 Concentration (ppm).



● Case Study 12-1. World Health Organization Guidelines for Ozone

The World Health Organization (WHO) is an international non-government organization (NGO) that acts as the directing and coordinating authority for health within the United Nations system. WHO's constitution, originating on April 7, 1948, states that its objective "is the attainment by all people of the highest possible level of health." It is responsible for providing leadership on global health matters, shaping the health research agenda, setting norms and standards, articulating evidence-based policy options, providing technical support to countries and monitoring and assessing health trends. Its mission is to combat disease, especially key infectious diseases and to promote the general health of the people of the world. The WHO flag features the Rod of Asclepius as a symbol for healing.

One primary focus area for WHO is air pollution, both indoor and outdoor. Air pollution is a major environmental health problem affecting everyone in developed and developing countries alike. WHO has published several reports on Air Quality Guidelines (AQG) [(WHO-Europe, 1987), (WHO-Europe, 2000), (WHO, 2006). These documents offer global guidance on reducing the health impacts of air pollution. The AQG applies worldwide and provides recommendations based on expert evaluation of current scientific evidence. The AQG - Global Update 2005 report revised limits from earlier reports for the concentration of particulate matter, ozone, nitrogen dioxide, and sulfur dioxide, applicable across all WHO regions (193 member states). The guidelines are not legal limits or regulatory, rather they provide the common background information to help nations and states to develop health and science based laws. No country is required to implement the WHO guidelines.

Key findings in the 2005 Air Quality Guidelines:

- *There are serious risks to health from exposure to PM and O_3 in many cities of the world.*
- *It is possible to derive a quantitative relationship between pollution levels and specific health outcomes (increased mortality or morbidity). The relationship allows insight into health improvements expected from a reduction in air pollution.*
- *Even relatively low concentrations of air pollutants correlate to adverse health effects.*

- *Poor indoor air quality may pose a risk to the health of over half of the world's population, including citizens in every member state.*
- *Significant reductions in exposure to air pollution due to lowering the concentrations of several of the most common air pollutants emitted during the combustion of fossil fuels. Such measures also reduce greenhouse gases and contribute to the mitigation of global warming.*

In addition to guideline values, the AQGs give interim targets for each outdoor air pollutant aimed at promoting a gradual shift from high to lower concentrations. Achieving these targets leads to significant reductions in risks for acute and chronic health effects from air pollution can be expected. Progress towards the guideline values, however, is the ultimate objective.

The WHO guidelines for Ozone (O_3) are 100 $\mu g/m^3$ for an 8-hour average. The previously recommended limit, 120 $\mu g/m^3$ 8-hour mean, was reduced based on new peer-reviewed scientific evidence showing conclusive associations between daily mortality and ozone levels occurring at ozone concentrations below 120 $\mu g/m^3$.

This evidence showed that the excessive ozone in the air can have a marked effect on human health causing breathing problems, triggering asthma, reducing lung function and causing lung diseases. The conclusion showed that the daily mortality rises by 0.3% and heart diseases by 0.4 %, per 10 $\mu g/m^3$ increase in ozone exposure.

● Case Study 12-2. Ozone Action Days

An Ozone Action Day, alternately called "Ozone Alert" or "Clean Air Alert," is called when the Air Quality Index (see chapter 1) gets into the unhealthy ranges (40 – 80 ppbv) for ozone. Different air pollution control agencies call them at different levels or set points. An action day is declared when the AQI is Moderate, or Code Yellow, if the levels are expected to approach Code Orange levels. In most places an action day is called when the AQI is forecast to be Code Orange - Unhealthy for Sensitive Groups (children, adults who are active outdoors, and people with lung disease, such as asthma). In other places, action days are called when the AQI is forecast to be Unhealthy, or Code Red. They can be declared by a local municipality, county or state, depending on the size of the affected region. The alert can be declared up to 24 hours before the ozone concentration is expected to exceed the action level. Local air quality experts (usually meteorologists) use air quality computer models, weather

data, measurements of pollution levels, and local experience to generate daily air pollution forecasts.

An ozone incident typically occurs during the summer when warm temperatures, sunny days, and the buildup of ozone precursors combine with a high-pressure system over an urban area. High temperatures enhance the rate of the ozone formation reactions. Sunshine increases the photo-chemical activity involving the precursors (NO_x and reactive carbon). High-pressure systems usually limit vertical mixing and have low-wind speeds that minimize the dispersal of pollutants and allow the concentrations of pollutants to build up.

An Ozone Action Day is a public notification designed to allow citizens to make informed choices about limiting their exposure to potentially harmful air pollution conditions. There are no laws requiring anyone to do or not do particular activities in the event of an action day. The declaring group typically provides a list of voluntary activities that can help limit or reduce the impact of the pollution incident.

Ozone Action Day Tips

- *Conserve electricity and set your air conditioner to a higher temperature.*
- *Choose a cleaner commute—share a ride to work or use public transportation. Bicycle or walk to errands when possible.*
- *Defer use of gasoline-powered lawn and garden equipment.*
- *Refuel cars and trucks after dusk.*
- *Combine errands and reduce trips.*
- *Limit engine idling.*
- *Use household, workshop, and garden chemicals in ways that keep evaporation to a minimum, or try to delay using them when expecting poor air quality.*

A daily US map showing the states and regions that have declared an Ozone Action Day is available at the US EPA AirNow website - http://www.airnow.gov/. Many other countries use similar systems to reduce harm from ozone air pollution.

12.1.5 Control

Tropospheric ozone is a secondary pollutant whose ambient concentration depends on the precursor concentrations of NO_x and reactive carbon (CO, CH_4, and NMVOCs). Since it is a secondary pollutant, control strategies focus on reducing emissions of the precursor pollutants. Chapter 10 discusses reductions of NO_x and Chapter 11 discusses reductions of reactive carbon. However, the photochemical production of ozone is non-linear with respect to the concentrations of the

precursors, so a simple reduction in one may not produce an associated reduction in ozone and could even cause an increase.

The current US-EPA modeling tool for forecasting ozone concentrations for Air Quality Index (AQI) decisions is the Community Multi-scale Air Quality (CMAQ) modeling system. This tool is useful for examining the effect of policy decisions on NOx and reactive carbon emissions linked to ambient ozone concentrations. It combines current peer-reviewed atmospheric science and air quality modeling with multi-processor computing techniques in an open-source framework to generate estimates of ozone, particles, toxics, and acid deposition. The latest information and a copy of the current CMAQ model is available for download from the Community Modeling and Analysis System (CMAS) Website – [http://www.cmascenter.org/].

The US-EPA's first-generation atmospheric models (1970's – 1990's) were created to predict the concentrations of single pollutants. The EPA had a regional acid deposition model, a regional model for predicting ozone, and a different regional model for particle pollution. These models tended to work well for a limited time and spatial scales. However, it was found that air pollution problems are dependent on multiple pollutants and that a better approach would require a single atmospheric model that incorporated all the pollutants together.

Starting in 1994 EPA began work on a "super model" framework that used data from other related models, in order to apply, combine, and interpret the previously separate information. The point of this model was to help scientists and policy makers at EPA determine how changes to proposed or existing air emission regulations would impact future air quality and provide benefit to public health. This super model simulates the atmospheric processes associated with air pollution by calculating solutions to mathematical model equations over a three-dimensional grid using millions of data points (e.g. position, temperature, pressure, humidity, wind speeds, concentrations and emissions of pollutants, availability of sunlight, and the effects of clouds and aerosols). It was first released for public use in 1998 after a concentrated development effort by researchers in EPA, NOAA, and the academic and private sectors.

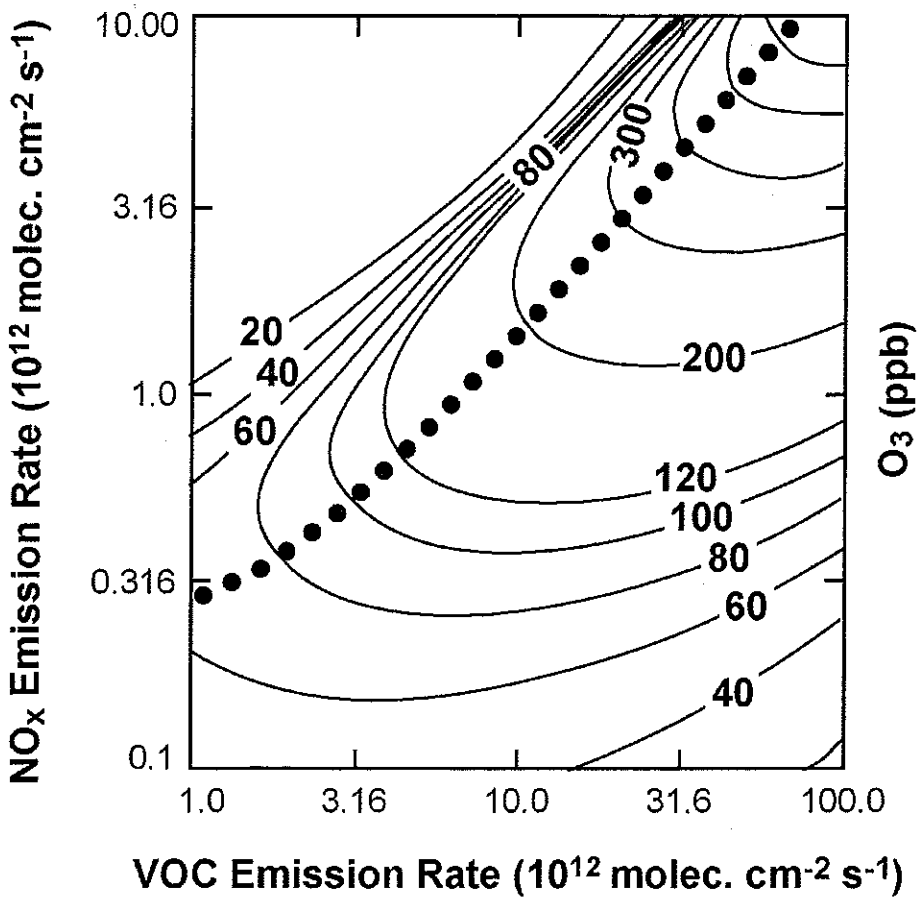
The CMAQ modeling system simulates the chemical and physical processes that occur in the atmosphere for all pollutants simultaneously. It combines three modeling components: meteorology, emissions, and chemistry-transport. The meteorology model is used to describe the state (e.g. temperature, pressure, humidity) and motions (horizontal and vertical wind speed and diffusion) of the atmosphere. The emissions model estimates the man-made and natural emissions injected into the atmosphere, including point sources (e.g. smoke stacks), and area sources (e.g. forests and crops). The chemical-transport model simulates the chemical transformations, including photolytic reactions, and ultimate fates of primary and secondary pollutants.

The grid resolutions and domain sizes for CMAQ range spatially and temporally over several orders of magnitude, and simulations can be performed to evaluate long-term (annual to multi-year) and short term (weeks to months) issues. CMAQ can be used for urban and regional scale model simulations because of its ability to handle a large range of spatial scales.

This model is extremely useful, but its complexity is beyond the scope of this text to use. However, a common relationship between the concentrations of NOx, and reactive carbon and ozone can be graphically represented using an Empirical Kinetic Modeling Approach (EKMA) plot (which originates from the first-generation models). It relates changes in the precursors to changes in the maximum ozone concentration and provides a simplified representation of possible effects from changes in the precursor pollutants. Figure 12-5 shows an EKMA ozone isopleth (ppb) as a function of a constant emission rate for NO_x and VOC (10^{12} molecules/(cm^2 •s)) in a zero-dimensional box model calculation (US-EPA, 2006b). The isopleths (solid lines) represent the peak ozone concentration during the three-day simulation period. The ridge line, shown by solid circles, shows the transition from NO_x-saturated (above) to NO_x-limited (below) conditions.

A zero-dimensional box model means that the calculations do not consider any spatial variations (calculations occur at a single point), the emissions of the precursors are held constant over the simulation, and that time increments are through three days. From the solution sets (NO_x and VOC emission rate variables) the maximum value of O_3 was chosen, even if it did not correspond to the same time between sets.

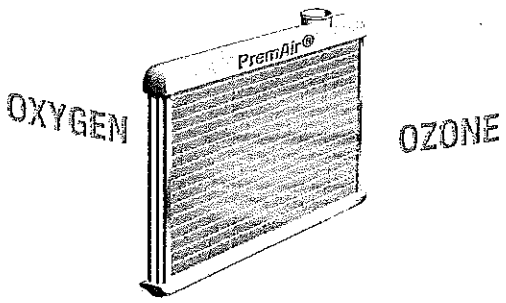
FIGURE 12-5. Calculated Ozone Isopleths Resulting from Constant Emission Rates of NO_x and VOCs.



This figure shows that reducing ozone concentrations requires different strategies depending on whether the atmosphere is VOC-limited or NO_x -limited. A VOC limited atmosphere (above the dotted line) requires reductions in VOC emissions to reduce ozone concentrations. A NO_x limited atmosphere (below the dotted line) requires reductions in NO_x emissions to reduce ozone concentrations. If VOCs were reduced in the NO_x-limited region it may have no effect, or it could cause an increase in the ozone concentration. Similarly, for the VOC limited region a reduction of the NO_x emission rate may not lead to a reduction in the formation of ozone. These results show how important it is to have good measurements of the actual concentrations of the precursors and to know their emission rates. It is also worth remembering that the atmospheric concentration of each precursor change with weather conditions and time of year. Therefore, there is no single strategy that works everywhere and at all times.

● **Case Study 12-3. Ozone Removal by BASF Catalyst's PremAir® Technology.** *Most air pollution control technology focuses on controlling emissions. Once emitted, people have relied on natural processes to remove or destroy the pollutants. The control of ground level ozone is very difficult because it is not an emitted pollutant; rather, it is the result of photochemical reactions involving NO_x and VOCs. Both have natural and anthropogenic emission sources and can travel hundreds of miles before reacting to form ozone. It has been the most difficult of the criteria air pollutants to control.*

BASF Catalyst has developed a commercial product that removes ozone from ground level air. The PremAir® catalyst can be applied to any heat exchange surface - such as car, bus and truck radiators, or stationary HVAC (Heating, Ventilation, and Air Conditioning) condensers. The catalyst uses the waste heat available from a radiator or condenser and uses it in the catalyzed destruction of ozone to form molecular oxygen.



The technology takes advantage of the huge volumes of air that are processed daily by both mobile and stationary heat exchange devices.

The treated automotive radiator is capable of removing up to 75% of the ozone in the air passing over it. The coating has no significant (less than 3%) impact on the perfor-

mance of the radiator. Durability tests from actual vehicle on-road fleet testing show that the catalyst retains up to 80% of its ability to destroy ozone after 100,000 miles.

PremAir catalysts have been successfully installed on over three million automotive radiators throughout the world. Manufacturers of Ultra Low Emission Vehicles (ULEV) and Super Ultra Low Emission Vehicles (SULEV) frequently use this technology. These vehicles receive an emission credit for an equivalent amount of VOCs, thus allowing greater flexibility in vehicle design. Air conditioners are also good candidates for the technology since they are often used in densely populated areas and when the outdoor temperature is high (both conditions correlate with high levels of ground level ozone).

The technology may be able to provide a positive benefit to the environment while being passive in the end user application. It does not require maintenance, upgrades, or repairs in normal use and lasts for the lifetime of the heat exchanger. However, no data exists to show that installation of this technology leads to an actual reduction in ambient ozone concentrations.

12.2 Stratospheric Ozone

12.2.1 Sources and Sinks

Ozone (O_3) is formed in the stratosphere by a reaction between molecular oxygen (O_2) and high-energy photons from the sun, a process called photolysis. This reaction occurs mainly over the tropics and mid-latitudes during summer when solar radiation is the most intense. Chapman first proposed the set of reactions that lead to the formation of stratospheric ozone (Chapman, 1930):

12.23 $O_2 + h\nu \rightarrow O + O$ $\lambda < 242$ nm

12.24 $O + O_2 + M \rightarrow O_3 + M$

12.25 $O + O_3 \rightarrow 2\ O_2$

12.26 $O_3 + h\nu \rightarrow O_2 + O$ $200 < \lambda < 360$ nm

Where: O is a free oxygen atom,
M is a catalyst particle,
$h\nu$ = energy from an absorbed photon (J),