

Introduction

The control of gaseous contaminants from industrial sources in the United States began with efforts to recover useful raw materials and products entrained in gas streams. Some of the high-efficiency pollutant control techniques in use today had their origin in the 1940s and 1950s as low-to-moderate efficiency collectors used strictly for process purposes. Starting in the 1950s and 1960s, control equipment for gaseous contaminants was used primarily for environmental purposes. The environmental control programs were stimulated by concerns about (1) possible health effects, (2) apparent crop and vegetation damage, and (3) the impact on buildings and other structures.

1.1 Introduction to Gaseous Contaminants

Gaseous contaminants can be divided into two main categories: primary and secondary pollutants. Primary pollutants are compounds that are emitted directly from the stack and/or process equipment of the source. Typical examples of primary pollutants include sulfur dioxide emissions from combustion sources and organic compound emissions from surface coating facilities. Secondary pollutants are gaseous and vapor phase compounds that form due to reactions between primary pollutants in the atmosphere or between a primary pollutant and naturally occurring compounds in the atmosphere. Important categories of secondary pollutants include ozone and other photochemical oxidants formed because of sunlight-initiated reactions of nitrogen oxides, organic compounds, and carbon monoxide. A summary of the main categories of gaseous contaminants is provided in the following list.

Primary Gaseous Contaminants

- Sulfur dioxide and sulfuric acid vapor
- Nitrogen oxide and nitrogen dioxide
- Carbon monoxide and partially oxidized organic compounds
- Volatile organic compounds and other organic compounds

<u>OBJECTIVES</u>	
<u>Terminal Learning Objective</u>	
At the end of this chapter, the student will be able to identify the basics of gaseous contaminants.	
<u>Enabling Learning Objectives</u>	
1.1	Distinguish between primary and secondary gaseous contaminants.
1.2	Identify sources of gaseous contaminants.
1.3	Describe the regulations that pertain to gaseous contaminants.
1.1	

- Hydrogen chloride and hydrogen fluoride
- Hydrogen sulfide and other reduced sulfur compounds (mercaptans, sulfides)
- Ammonia

Secondary Gaseous Contaminants

- Nitrogen dioxide
- Ozone and other photochemical oxidants
- Sulfuric acid

There is not a sharp dividing line between primary and secondary gaseous contaminants. For example, nitrogen dioxide and sulfuric acid are in both groups. Many primary gaseous contaminants can participate in atmospheric reactions to form secondary reaction products.

Sulfur Dioxide and Sulfuric Acid Vapor

Sulfur dioxide (SO₂) is a colorless gas formed primarily during the combustion of a sulfur-containing fuel, such as coal, No. 6 oil, or sulfur-containing industrial waste gases. Once released to the atmosphere, sulfur dioxide reacts slowly because of photochemically initiated reactions and reactions with cloud and fog droplets, at rates of between approximately 0.1% and 3% per hour. These atmospheric reactions yield sulfuric acid, inorganic sulfate compounds, and organic sulfate compounds. A major fraction of sulfur dioxide is ultimately captured on vegetation and soil surfaces because of adsorption and absorption. These processes are collectively termed *deposition*. Rates of deposition are not accurately quantified and vary both regionally and seasonally. Sulfur dioxide is moderately soluble in water and is a strong irritant, due in part to its solubility and tendency to form sulfurous acid following absorption in water. SO₂ is one of the seven criteria pollutants subject to National Ambient Air Quality Standards (NAAQS).

During the combustion of sulfur-containing fuels, approximately 95% of the sulfur is converted to sulfur dioxide, while 0.5% to 2% of the fuel sulfur is converted to sulfur trioxide, SO₃. Sulfur trioxide remains in the vapor state until temperatures decrease below approximately 600°F (300°C). At this temperature, sulfur trioxide reacts with water to form sulfuric acid as indicated in Reaction 1-1.



Because of its corrosiveness, it is important to keep gas streams at temperatures above the sulfuric acid dew point. Damage to air pollution control equipment, ductwork, and fans can occur if the gas temperature falls below the sulfuric acid dew point in localized areas.

Nitric Oxide and Nitrogen Dioxide

These two compounds, collectively referred to as NO_x , are formed during the combustion of all fuels. They are also released from nitric acid plants and other industrial processes involving the generation and/or use of nitric acid. The term “ NO_x ” does not include nitrous oxide (N_2O), which is emitted in small quantities from some processes.

Three complex chemical mechanisms are responsible for NO_x formation: (1) thermal fixation of atmospheric N_2 , (2) oxidation of organic nitrogen compounds in the fuel, and (3) reaction with partially oxidized compounds within the flame. These mechanisms are referred to as thermal, fuel, and prompt NO_x , respectively.

Nitric oxide (NO) is an odorless gas that is insoluble in water. Nitrogen dioxide (NO_2) is moderately soluble in water and has a distinct reddish-brown color. This compound contributes to the brown haze that is often associated with photochemical smog conditions in urban areas. At low temperatures, such as those often present in ambient air, nitrogen dioxide can form a dimer compound (N_2O_4). Both compounds, but particularly NO_2 , are associated with adverse effects on the respiratory tract. NO_2 has been regulated since 1971 as one of the seven criteria pollutants subject to National Ambient Air Quality Standards (NAAQS).

The ambient concentrations of NO and NO_2 are usually well below the NO_2 NAAQS. In fact, at the present time, all regions of the country are in compliance with the NO_2 NAAQS. This is due to the rapid photochemically initiated reactions and liquid phase reactions (clouds and fog droplets) that result in the conversion of NO_x in the atmosphere to secondary reaction products. In fact, NO_2 is the main chemical compound responsible for the absorption of the ultraviolet light that drives photochemical reactions.

Carbon Monoxide and Other Partially Oxidized Organic Compounds

Carbon monoxide is a partially oxidized compound that results from incomplete combustion of fuel and other organic compounds. It forms when either the gas temperature is too low or the oxygen concentration is insufficient to promote complete oxidation to carbon dioxide.

Carbon monoxide is a very stable, difficult-to-oxidize compound. It is more difficult to complete the oxidation of CO to CO_2 than to complete the oxidation of any partially oxidized organic compound. Temperatures of 1800°F (1000°C) or greater are required to oxidize CO .

Carbon monoxide is colorless, odorless, and insoluble in water. It is a chemical asphyxiant with significant adverse health effects at high concentrations. Carbon monoxide readily participates in photochemically initiated reactions that result in smog formation. It is emitted from automobiles, trucks, boilers, and industrial furnaces.

Partially oxidized compounds (POCs) refer to a broad range of species formed during the combustion process, including polyaromatic compounds, unsaturated compounds, aldehydes, and organic acids. Some POCs readily condense on the surface of particulate matter while others remain in the gas phase. Combustion conditions used to minimize the formation of NO_x , such as

reducing the excess O₂ concentration, actually promote the formation of CO and POCs.

Volatile Organic Compounds or Other Organic Compounds

Volatile organic compounds (VOCs) are organic compounds that can volatilize and participate in photochemical reactions once released to the ambient air. Almost all of the several thousand organic compounds used as solvents and as chemical feedstock in industrial processes are classified as VOCs. The few organic compounds that are *not* considered VOCs because of their lack of photochemical reactivity are listed in Table 1-1.

Table 1-1. Organic compounds <u>NOT</u> classified as VOCs.
Methane
Ethane
Methylene chloride (dichloromethane)
1,1,1-trichloroethane (methyl chloroform)
Trichlorofluoromethane (CFC-11)
Dichlorodifluoromethane (CFC-12)
Chlorodifluoromethane (CFC-22)
Trifluoromethane (FC-23)
1,2-dichloro 1,1,2,2-tetrafluoroethane (CFC-114)
Chloropentafluoroethane (CFC-115)
1,1,1-trifluoro 2,2-difluoroethane (HCFC-123)
1,1,1,2-tetrafluoroethane (HCFC-134a)
1,1-dichlorofluoroethane (HCFC-141b)
1-chloro 1,1-difluoroethane (HCFC-142b)
2-chloro 1,1,1,2-tetrafluoroethane (HCFC-124)
Pentafluoroethane (HFC-125)
1,1,2,2-tetrafluoroethane (HFC-134)
1,1,1-trifluoroethane (HFC-143a)
1,1-difluoroethane (HFC-152a)
Cyclic, branched, or linear completely fluorinated alkanes
Cyclic, branched, or linear completely fluorinated ethers with no unsaturations

Table 1-1 (continued). Organic compounds <u>NOT</u> classified as VOCs.
Cyclic, branched, or linear completely fluorinated tertiary amines with no unsaturations
Sulfur containing perfluorocarbons with no unsaturations and with sulfur bonds only to carbon and fluorine
Perchloroethylene (addition proposed by U.S. EPA)
Perchloroethylene (tetrachloroethylene)
Parachlorobenzotrifluoride (PCBTF)
Volatile methyl siloxane (VMS)
Acetone

The dominant source of VOC emissions is the vaporization of organic compounds used as solvents in industrial processes, but VOCs are also released during surface coating operations, painting, gasoline distribution, and synthetic organic chemical manufacturing.

VOC emissions may be categorized as either contained or fugitive. Contained VOCs are those that are captured in hoods, penetrate through the air pollution control equipment, and are released from the stack. Fugitive emissions consist of those that escape from process hoods as well the numerous small leaks from pumps, valves, and other process equipment.

Approximately 200 specific organic compounds and classes of compounds that have known adverse health effects are regulated as hazardous air pollutants (HAPs). These compounds are subject to Maximum Achievable Control Technology (MACT) standards promulgated by EPA. A partial list of the more common hazardous air pollutants is presented in Table 1-2.

Table 1-2. Examples of organic HAPs.			
Compound	CAS Number	Compound	CAS Number
Acetaldehyde	75070	Methylene chloride	75092
Acetonitrile	75058	Methyl ethyl ketone	78933
Acrolein	107028	Methyl isocyanate	624839
Acrylonitrile	107131	Naphthalene	91203
Aniline	62533	Nitrobenzene	98953
Benzene	71432	Phenol	108952
1,3, Butadiene	106990	Phosgene	75445
Carbon disulfide	75150	Phthalic anhydride	85449
Chlorobenzene	108907	Styrene	100425
Chloroform	67663	Tetrachloroethylene	127184
Ethyl benzene	100414	Toluene	108883
Ethylene oxide	75218	2,4 Toluene diisocyanate	584849
Ethylene glycol	107211	1,2,4 Trichlorobenzene	120821
Formaldehyde	50000	Trichloroethylene	79016
Hexane	110543	Xylenes	95476
Methanol	67561		

Hydrogen Chloride and Hydrogen Fluoride

Hydrogen chloride (HCl) and hydrogen fluoride (HF) are inorganic acid gases that may be released from processes such as waste incinerators, fossil fuel-fired boilers, chemical reactors, or ore-roasting operations. They are also generated and released from air pollution control systems in which chlorine- or fluorine-containing organic compounds are oxidized. They are gases at the normal stack concentrations; however, at high concentrations, HCl can nucleate to form submicrometer acid mist particles.

Both HCl and HF are extremely soluble in water and are strong irritants. Both compounds can cause adverse health effects. HCl and HF are regulated as hazardous air pollutants.

The quantities of HCl and HF formed during waste incineration and fossil fuel combustion are directly related to the concentrations of chlorine and fluorine in the waste or fuel being fired. Essentially all of the chlorine and fluorine atoms are converted to HCl or HF as long as sufficient hydrogen is present from hydrocarbons or water vapor in the gas stream. Very few of the chlorine or fluorine atoms remain in the ash of combustion processes.

Hydrogen Sulfide and Other Total Reduced Sulfur Compounds

Hydrogen sulfide (H_2S) is emitted from a number of metallurgical, petroleum, and petrochemical processes. Fugitive emissions of H_2S occur from sour natural gas wells and certain petrochemical processes. H_2S is a highly toxic chemical asphyxiant. Despite its strong rotten-egg odor, it is often difficult to detect at high concentrations due to rapid olfactory fatigue. H_2S is highly soluble in water and can be easily oxidized to form sulfur dioxide. Total reduced sulfur compounds (TRSs) are emitted primarily from kraft pulp mills and consist primarily of the following four chemicals.

- Hydrogen sulfide, H_2S
- Methyl mercaptan, CH_3SH
- Dimethyl sulfide, $(\text{CH}_3)_2\text{S}$
- Dimethyl disulfide, $(\text{CH}_3)_2\text{S}_2$

All have extremely strong and unpleasant odors. Facilities generating TRS compounds have been subject to source-specific control regulations since the early 1970s due to the associated odor problems. All of these compounds are water soluble. They all participate readily in atmospheric reactions that eventually yield sulfur dioxide as the main reaction product. TRS compounds are usually controlled by oxidation.

Ammonia

Ammonia (NH_3) is a common chemical used in a large number of synthetic organic chemical manufacturing processes. Emissions of ammonia from such sources are usually quite small and are well below the natural emissions from microbial activity. Ammonia is not considered to be toxic at the levels generated by anthropogenic or natural emissions and is not regulated as a hazardous pollutant.

Ammonia is of interest in Course 415 primarily because it is a reactant in two main types of NO_x control systems. A small fraction of the ammonia fed to these NO_x control systems can be emitted to the atmosphere, and these emissions are regulated in some states.

Ozone and Other Photochemical Oxidants

Ozone (O_3) is an oxidant that forms in the troposphere because of the photochemically initiated reactions of nitrogen oxides, volatile organic compounds, and carbon monoxide. Course 415 does not explicitly cover the control of ozone because it is a secondary pollutant. Control of ozone is achieved by the control of precursor compounds such as NO_x , VOCs, and CO.

The general cycle of pollutant concentrations associated with photochemical reactions is illustrated in Figure 1-1. The reactions typically begin quickly in the mid-to-late morning following the increase in concentrations of NO_x , organic compounds, and CO from motor vehicles and other sources. Photochemically initiated reactions rapidly convert NO to NO_2 . The formation of NO_2 further

stimulates the photochemical smog-forming reactions because nitrogen dioxide is very efficient in absorbing ultraviolet light.

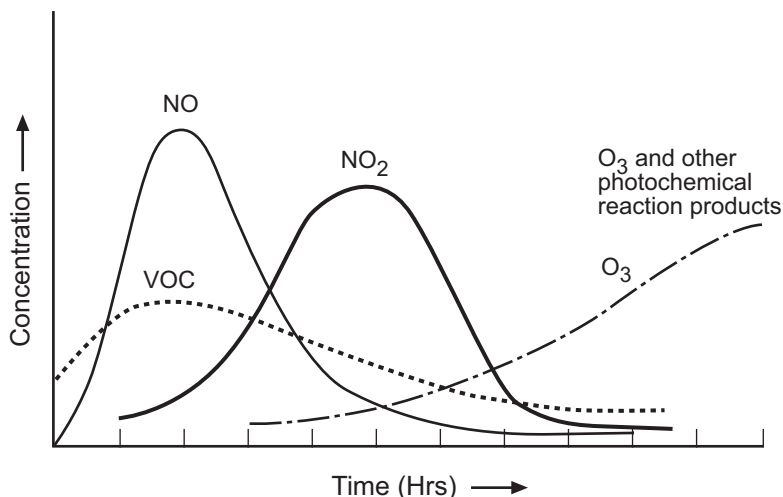


Figure 1-1. Pollutant concentration profiles due to photochemical reactions.

As the day proceeds, the NO_2 concentration peaks and then decreases as it is consumed to form particulate matter and vapor phase nitrates. As the NO_2 concentration drops, the levels of ozone rise rapidly. Along with the increase in ozone, the levels of various partial oxidation products also increase. Some of the photochemical reaction products are in the form of particulate matter that scatters light.

The formation of ozone is greatest during the “ozone season,” usually defined as May through September. The intensity of sunlight for the photochemically initiated reactions is highest during this time period, and the high temperatures promote thermal reactions associated with the photochemical reactions.

Ozone can also form, to a limited extent, in clean rural environments. The “pollutants” involved in these reactions are low levels of organic compounds emitted from vegetation and low levels of NO_x emitted from natural biological activity. While the photochemical reactions are similar to those found in polluted urban areas, the concentrations of rural ozone are limited by the low concentrations of NO_x usually present.

In the stratosphere, ozone forms naturally from the irradiation of molecular oxygen by sunlight. The presence of ozone in the stratosphere is beneficial because it absorbs ultraviolet radiation from the sun. The stratospheric ozone concentrations are decreasing over North America because of the presence of ozone-depleting chlorinated and fluorinated organic compounds and nitrous oxide, compounds that are not especially reactive near the Earth's surface. Once these compounds are transferred convectively to the stratosphere, they can initiate free radical chain reactions that reduce the equilibrium concentrations of

ozone. The depletion of ozone in the stratosphere is not within the scope of this course.

The control of precursor gases, such as NO_x, to minimize ground level ozone concentrations, will *not* have an adverse effect on the beneficial ozone levels in the stratosphere. The formation mechanisms for ozone in the stratosphere are different from those in the troposphere.

Mercury

Mercury enters the environment as a result of both natural and human activities. While elemental mercury is toxic to humans, methylmercury (CH₃Hg⁺) is the compound of most concern. Methylmercury is formed from other forms of mercury by microbial action in sediments and soils, and is taken up by aquatic organisms and bioaccumulates in the aquatic food chain.

Anthropogenic mercury enters the atmosphere primarily due to the combustion of coal and other fossil fuels that contain trace quantities of mercury. Other significant sources of mercury emissions include certain chlor-alkali chlorine manufacturing processes, mining operations, metal refining, and products that contain elemental mercury, such as batteries, lamps, and thermometers.

EPA has focused most of its mercury reduction efforts on large point source emissions from chlor-alkali facilities and combustion sources ranging from power plants and industrial boilers to hazardous waste and medical incinerators. Significant reductions in mercury emissions have already been made, and total air emissions in 1999 were estimated to be only about one-half of the 1990 emissions. The greatest emission reductions during that period occurred from municipal waste and medical waste incinerators. However, little progress was made during that time in reducing emissions from power plants and industrial boilers. In 2005 EPA promulgated the Clean Air Mercury Rule, which (among other things) required a 70% reduction in mercury emissions from coal-fired power plants by 2018. This rule was subsequently struck down by a federal court and, at the time of this writing (March 2009), there are no federal regulations concerning mercury emissions from coal-fired power plants.

Greenhouse Gases

Greenhouse gases trap heat in the atmosphere. In the absence of greenhouse gases, the earth would be too cold to sustain human life. However, in the opinion of many experts, the increasing concentrations of greenhouse gases (principally CO₂) since the beginning of the industrial revolution have led to global warming.

The most important greenhouse gases that enter the atmosphere as a result of human activity are:

Carbon Dioxide. CO₂ is a primary product from the combustion of fossil fuels (coal, oil, and natural gas), solid waste, and trees and other wood products. Significant amounts are also liberated during the manufacture of cement and other products. CO₂ is removed from the atmosphere by plants as part of the natural biological carbon cycle and by dissolution into the oceans. In recent

times, the rate of emissions is exceeding the rate of removal, and the average CO₂ concentration has been increasing at a rate of from 1 to 3 ppm/yr.

Methane. CH₄ is discharged to the atmosphere during the production and transportation of coal, oil, and natural gas. CH₄ emissions also result from livestock and other agricultural activities and from the decay of organic waste.

Nitrous Oxide. N₂O is emitted from the combustion of fossil fuels, although the quantities are much smaller than the emissions of NO and NO₂. The majority of N₂O emissions result from agricultural activities.

Fluorinated Gases. Hydrofluorocarbons, perfluorocarbons, and sulfur hexafluoride are greenhouse gases that are emitted from a number of industrial processes. A large fraction of the fluorinated gases were introduced as substitutes for stratospheric ozone-depleting chlorinated gases (CFCs and HCFCs). The absolute quantities are small, although their greenhouse warming potential is high.

Different greenhouse gases have widely different impacts, which are measured by the *Global Warming Potential (GWP)*. Among other factors, the GWP depends on the average atmospheric lifetime of individual greenhouse gases. CO₂ was chosen as the reference point and assigned a GWP of 1.0. Estimated atmospheric lifetimes and GWPs of the major greenhouse gases are summarized in the following table.

Table 1-3. Global warming potentials (GWP) and atmospheric lifetimes (years).		
Gas	Atmospheric Lifetime	100-Year GWP
Carbon dioxide, CO ₂	50-200	1
Methane, CH ₄	12±3	21
Nitrous oxide, N ₂ O	120	310
Fluorinated gases as a group	1.5–209	140–11,700

1.2 Emission Rates and Sources of Gaseous Contaminants

Annual Emission Rates

The gaseous contaminants emphasized in this course include sulfur dioxide, nitrogen oxides, and organic compounds (including VOCs). Mercury and greenhouse gases are included for the first time in this edition of the course. Emissions data from the EPA emissions inventory for SO₂, NO_x, and VOC, for the period 1970–2007, are shown in Figure 1-2. Significant emissions reductions in each pollutant have been achieved. On a percentage basis, the reductions range from 59% for SO₂ to 47% for VOC to 37% for NO_x. These reductions

were achieved in spite of population increases and economic growth during the time period.

SO₂ emission reductions have been reasonably steady throughout the period. NO_x emissions were relatively constant from 1970 to 1995, while reductions have accelerated since that time. VOC emissions decreased steadily from 1970 to 2000, but there was a significant increase between 2000 and 2005. However, the increase was reversed between 2005 and 2007.

Controls on the release of mercury to the atmosphere are just now being implemented and emissions data are relatively scarce. EPA estimates that the annual emission rate of 220 short tons per year in 1990 was reduced to 115 short tons per year by 1999.

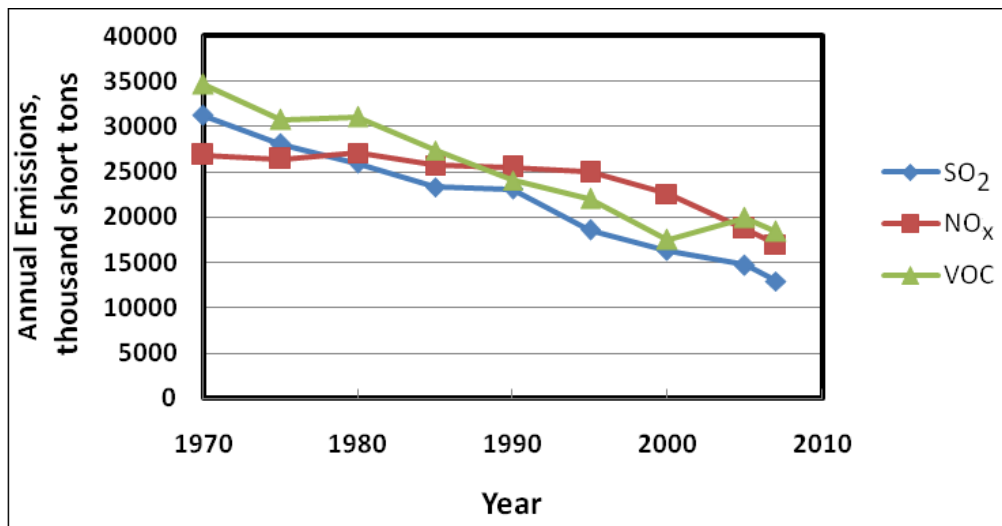


Figure 1-2. SO₂, NO_x, and VOC emissions history.

Estimated annual emissions of greenhouse gases between 1990 and 2006 are shown in Figure 1-3. The units on the ordinate are teragrams of CO₂ equivalent (1 teragram = 10¹² g). That is, emissions of CH₄ and other greenhouse gases are multiplied by their global warming potential so that the total emissions are on a CO₂-equivalent basis. We see that CO₂, with the smallest GWP of 1, is easily the most important greenhouse gas, followed by CH₄, N₂O, and the fluorinated compounds. To put the numbers into somewhat better perspective, the 1990 emissions rate of 6.14 Tg is the equivalent of 6.14 x 10⁶ short tons. The overall data show an approximate 15% increase in GHG emissions during the 1990–2006 period.

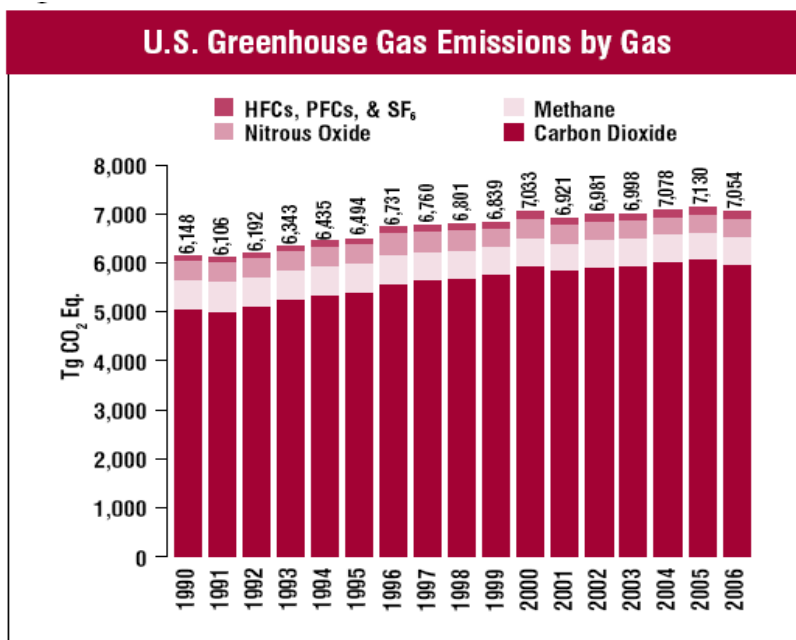


Figure 1-3. Estimated greenhouse gas emissions in terms of CO₂ equivalent.

Emission Source Categories

In this section, the total emissions described in the previous section are subdivided into source categories, and current (2007) results are compared to the 1970 values for SO₂ (Table 1-4), NO_x (Table 1-5), and VOCs (Table 1-6).

Table 1-4 shows that 1970 SO₂ emissions were dominated by fuel combustion in electric utilities, followed by metal processing and fuel combustion in industrial boilers. The three fuel combustion categories – electric utilities, industrial, and other – accounted for about 75% of the total. Highway and off-highway vehicles, in contrast, accounted for only about 2% of the total.

All source categories (except “other”) experienced large decreases between 1970 and 2007, with the largest percentage decrease (95%) associated with metals processing. Electric utility emissions decreased by 48% during that time, but remained the largest source category. The reductions, which were accomplished by the installation of flue gas desulfurization processes and by switching to lower sulfur content fuels, occurred in spite of a large increase in demand for electricity during that time period.

Table 1-4. SO₂ emissions by source category, 1970 and 2007.				
Source Category	1970		2007	
	Thousands of Short Tons	Percent of Total	Thousands of Short Tons	Percent of Total
Fuel combustion, electric utilities	17,398	56	8973	69
Fuel combustion, industrial	4568	15	1705	14
Fuel combustion, other	1490	5	577	4
Chemical and allied products	591	2	258	2
Metals processing	4775	15	213	2
Petroleum and related industries	881	3	232	2
Other industrial processes	846	3	323	2
Highway vehicles	273	1	91	1
Off-highway vehicles	278	1	396	3
Other	118	0	157	1
Total	31,218	101	12,925	100

NO_x emissions reductions, shown in Figure 1-2, while significant, are less impressive than the reductions achieved for SO₂. Most of the overall reduction of 37% has occurred since 1995. These trends reflect the importance of automobiles to NO_x emissions, and the relative difficulty of controlling NO_x emissions from electric utility plants compared to SO₂ emissions. Table 1-5 compares NO_x emissions from 1970 and 2007 by source category. Highway vehicles were the largest source of NO_x in both 1970 and 2007, but off-highway vehicles supplanted electric utilities as the second most significant source in 2007. On an overall basis, combined combustion operations from stationary and mobile sources accounted for over 95% of the total NO_x emissions in 2007. The largest percentage decrease between 1970 and 2007 came in the category of highway vehicles, while off-highway vehicles were the only category showing an absolute increase in emissions between 1970 and 2007.

Table 1-5. NO_x emissions by source category, 1970 and 2007.

Source Category	1970		2007	
	Thousands of Short Tons	Percent of Total	Thousands of Short Tons	Percent of Total
Fuel combustion, electric utilities	4900	18	3331	20
Fuel combustion, industrial	4325	16	1941	11
Fuel combustion, other	836	3	733	4
Highway vehicles	12,624	47	5563	33
Off-highway vehicles	2652	10	4164	24
Other	1545	6	1286	8
Total	26,882	100	17,025	100

VOC emissions, shown in Figure 1-2, decreased significantly from 1970 to 2000, but then increased by about 5% between 2000 and 2005 before dropping off again between 2005 and 2007. Overall, between 1970 and 2007, the VOC emissions decreased by 47%. Table 1-6 compares VOC emissions during 1970 and 2007 by source category. Highway vehicles followed by solvent utilization were the largest source categories in 1970. Emissions from highway vehicles were due primarily to evaporative emissions from gasoline tanks. By 2007, however, reductions in automobile evaporative losses had decreased to the point that solvent utilization had become the largest source, and highway vehicle losses were effectively tied with the “Other” source category for second place. Unlike SO₂ and NO_x emissions, combustion processes contribute only a small amount of the VOC emissions.

Table 1-6. VOC emissions by source category, 1970 and 2007.				
Source Category	1970		2007	
	Thousands of Short Tons	Percent of Total	Thousands of Short Tons	Percent of Total
Fuel combustion, electric utilities	30	0	49	0
Fuel combustion, industrial	150	0	141	1
Fuel combustion, other	541	2	1436	8
Chemicals manufacture	1341	4	238	1
Petroleum industry	1194	3	580	3
Solvent utilization	7174	21	4249	23
Storage and transport	1954	6	1354	7
Waste disposal & recycling	1984	6	381	2
Highway vehicles	16910	47	3602	20
Off-highway vehicles	1616	5	2650	14
Other	1765	5	3743	20
Total	34,659	99	18,423	99

The most important sources of mercury emissions in 1990 were municipal solid waste incinerators, coal-fired electric utility boilers, and medical waste incinerators. Each of these categories contributed about 25% of the total. Relatively small additional mercury emissions were contributed by institutional boilers, chlorine production, hazardous waste incineration, gold mining, and “other.” By 1999, mercury had been largely eliminated from municipal waste and medical waste incinerators, and coal-fired utility boilers contributed about 40% of the total estimated emissions of 115 short tons.

CO₂, the dominant greenhouse gas, was associated almost entirely with fuel combustion, both in stationary and mobile sources. CH₄ is emitted during the production and transport of coal, oil, and natural gas, by livestock and other agricultural practices, and by the decay of organic materials in municipal solid waste landfills. Nitrous oxide is emitted from agricultural and industrial activities, and small amounts are emitted during combustion of fossil fuels. The fluorinated gases, many of which were introduced as substitutes for ozone-depleting

chlorinated compounds, are emitted in small quantities from a number of industrial sources.

1.3 Gaseous Contaminant Regulations

From 1950 through 1970, gaseous pollutant control regulations were enacted by state and local agencies for contaminants such as SO₂, VOCs, and HF. These regulations were aimed at alleviating localized health and welfare effects relating to these emissions. The environmental awareness that began to increase during the 1950s and 1960s culminated in the enactment of the Clean Air Act of 1970 (CAA). This act strengthened the federal program and was associated with the formation of the U.S. EPA from a variety of agencies sharing environmental responsibility before this time. The CAA substantially increased the pace of gaseous contaminant control. Since 1970, a myriad of regulations have been promulgated that apply, in one way or another, to gaseous emissions. The following paragraphs provide only a brief overview of the most important laws and regulations that have been developed.

In 1971, the newly formed EPA promulgated primary and secondary National Ambient Air Quality Standards (NAAQS) for sulfur dioxide, nitrogen oxides, photochemical oxidants, and carbon monoxide. These standards were based on the available ambient air monitoring and health/welfare effects research data. The country was divided into a number of Air Quality Control Regions, each of which was intended to reflect common air pollution problems. Areas whose measured ambient concentrations exceeded the NAAQS levels were labeled as nonattainment areas for the specific gaseous contaminant. Nonattainment areas were required to devise a set of emission regulations and other procedures that would reduce the particular pollutant concentration in the ambient air to levels below the NAAQS specified limit.

Both primary and secondary standards have been specified for certain compounds. The primary standards are more restrictive and are designed to protect human health. The secondary standards are intended to reduce adverse material effects, such as crop damage and building soiling. Individual states are responsible for developing control strategies for the achievement of the NAAQS as part of the State Implementation Plan (SIP) required by the Clean Air Act. Emission regulations were adopted by many state and local agencies to ensure that the NAAQS would be met.

These emission limitations take different forms in different areas. For example, in some areas, SO₂ emissions are limited by specifying a maximum sulfur content (e.g., ≤ 1% sulfur by weight) on the fuel being burned. In other instances, emission limitations for SO₂ and NO_x are based on an allowable mass per unit of heat input (e.g., 0.1 lb NO_x/MM Btu) or strictly on a concentration basis (e.g., 500 ppm). Emissions of VOCs are restricted based on the allowable mass per unit time (e.g., pounds per hour) or a VOC content per unit of coating.

Regulations were adopted to control process-related fugitive emissions. Because of the diversity of these sources and the difficulty of measuring these emissions, these regulations have taken many forms, including (1) required work

practices, (2) leak detection and repair programs, and (3) hood capture efficiency requirements.

Regulations adopted under SIPs apply to *existing* sources within the state. There are substantial differences in the stringency of the regulations from state to state, depending on the contaminant control strategy believed necessary and advantageous to achieve the NAAQS.

The Clean Air Act also stipulated that *New Source Performance Standards (NSPS)* were to be developed on a nationwide basis to apply to all new (and substantially modified) sources. The purpose of the NSPS was to ensure continued improvements in air quality as new sources replaced existing sources. These NSPS were adopted by EPA on a source category-by-category basis. Sources subject to these regulations are required to install air pollution control systems that represent the “best demonstrated technology” for that particular source category. The first set of NSPS standards (often termed Group I) included emission limitations for SO₂ and NO_x from large combustion sources. EPA has included continuous monitoring requirements in many of the new and revised NSPS standards applicable to SO₂ and NO_x emissions.

The CAA also authorized the promulgation of especially stringent regulations for pollutants considered to be highly toxic or hazardous. EPA was charged with identifying these pollutants and developing appropriate regulations to protect human health. The set of regulations that apply to toxic or hazardous chemicals is titled the National Emission Standards for Hazardous Air Pollutants (NESHAPS). Because of regulatory complexities occurring from 1971 to 1990, only a few of these were promulgated, and none of these involved gaseous contaminants. The Clean Air Act Amendments of 1990 required a major revision and expansion of NESHAPS. Regulations have been developed for 188 specific compounds and classes of compounds, including many that are normally in gaseous form. Sources subject to NESHAPS are required to limit emissions to levels consistent with *Maximum Achievable Control Technology (MACT)*. The MACT requirements are based on technology currently used by best performing sources within that category.

Before construction begins, new sources (or major modifications to existing sources) are required to undergo a New Source Review (NSR) and receive a pre-construction permit. In areas where NAAQS are currently satisfied, the permit is based on *Prevention of Significant Deterioration (PSD)* requirements. PSD requires the use of Best Available Control Technology (BACT). BACT is determined on a case-by-case evaluation that considers energy, environmental, and economic impact. In areas where the NAAQS are not satisfied, the NSR permit requires that new emissions must be offset with emission reductions from other sources and to install *Lowest Achievable Emissions Rate (LAER)* technology. Under LAER the applicant must achieve (1) the most stringent emission limitation in the SIP for a similar source or (2) the most stringent emission achieved in practice.

In 1997, EPA added a new NAAQS applicable to particulate matter having a diameter equal to or less than 2.5 μm (termed PM_{2.5}). EPA concluded that the PM_{2.5} NAAQS were needed because health effects research indicated that particulate matter in this size category is most closely associated with adverse health effects. Control of PM_{2.5} is directly relevant to APTI 413, Control of Particulate Emissions, but it is also important to gaseous emission control

because atmospheric chemistry research indicates that the atmospheric reactions of SO₂, NO_x, VOCs and CO have a significant role in the formation of PM_{2.5} particles. The PM_{2.5} regulations will continue to drive gaseous contaminant control in the future.

Mercury is one of the 188 compounds defined as a hazardous or toxic material and is, therefore, subject to NESHAP regulations. In addition, there are mercury-specific laws and regulations. For example, the Mercury Containing and Rechargeable Battery Management Act of 1996 required phasing out the use of mercury in batteries. The Resource Conservation and Recovery Act (RCRA) set emission limits for the incineration of mercury-containing hazardous waste. The Clean Air Mercury Rule, issued in 2005, and subsequently overturned by federal court action, was meant to establish the first-ever limitations on mercury emissions from coal-fired power plants. No specific limitations on mercury from coal-fired power plants currently exist (as of March 2009) as a result of the court action.

At the time of this writing (March 2009), there are no U.S. limitations on greenhouse gas emissions. However, the anticipation of future regulations has spurred research in the use of non-carbon energy sources and in the capture and sequestration of carbon from fossil fuels.

New Source Performance Standards

New source performance standards have been promulgated for about 70 industrial categories. Because of their legal standing, the standards are quite complex and require a lawyer for full interpretation. An abbreviated and simplified version of the NSPS for fossil fuel-fired electric power generation facilities is presented in Table 1-7. This is meant only to provide a rough guide for this course and should not be used in actual work. Complete New Source Performance Standards may be found in the Code of Federal Regulations, 40 CFR Part 60 Subpart Da.

The performance standard for SO₂ from any fuel type is 1.2 lb_m/10⁶ Btu heat input, along with 90% reduction from the amount that would be emitted in the absence of controls. If, however, the emission rate is less than 0.6 lb_m/10⁶ Btu heat input, only 70% reduction from the uncontrolled rate is required. Separate NO_x emission standards and reduction requirements have been promulgated for different fuel types. The different emission standards generally reflect differences in the nitrogen content of the fuel.

Table 1-7. New source performance standards for fossil fuel-fired electric power generating facilities.			
Category	Fuel Type	Emission Limit	Reduction Requirement
Particulate matter	Solid	0.03 lb _m /10 ⁶ Btu	99%
	Liquid	0.03 lb _m /10 ⁶ Btu	70%
SO ₂	Any	1.2 lb _m /10 ⁶ Btu	90%
		<0.6 lb _m /10 ⁶ Btu	70%
NO _x	Solid	0.5 lb _m /10 ⁶ Btu	65%
	Liquid	0.3 lb _m /10 ⁶ Btu	30%
	Gas	0.2 lb _m /10 ⁶ Btu	20%

National Ambient Air Quality Standards

National ambient air quality standards, shown in Table 1-8, have been promulgated for seven criteria pollutants. Separate standards exist for particulate matter depending on particle size. PM_{2.5} refers to particles with diameters less than 2.5 microns, while PM₁₀ refers to particles with diameters less than 10 microns. SO₂ has its own primary and secondary standards, while the primary and secondary standards for the other materials are the same. Primary standards are designed to protect public health, including the health of sensitive populations such as asthmatics, children, and the elderly. Secondary standards protect public welfare, including protection against decreased visibility and damage to animals, crops, vegetation, and buildings. These standards also have legal meaning, and their interpretation can be quite complex as indicated by the extensive list of explanatory material below the table. Notice that some of the standards have changed with time as continued research expands the knowledge base concerning the pollutant effects.

Table 1-8. National ambient air quality standards.

Pollutant	Primary Standards		Secondary Standards	
	Level	Averaging Time	Level	Averaging Time
Carbon Monoxide	9 ppm (10 µg/m ³)	8-hour ⁽¹⁾	None	
	35 ppm (40 µg/m ³)	1-hour ⁽¹⁾		
Lead	0.15 µg/m ³ ⁽²⁾	Rolling 3-Month Average	Same as Primary	
	1.5 µg/m ³	Quarterly Average	Same as Primary	
Nitrogen Dioxide	0.053 ppm (100 µg/m ³)	Annual (Arithmetic Mean)	Same as Primary	
Particulate Matter (PM ₁₀)	150 µg/m ³	24-hour ⁽³⁾	Same as Primary	
Particulate Matter (PM _{2.5})	15.0 µg/m ³	Annual ⁽⁴⁾ (Arithmetic Mean)	Same as Primary	
	35 µg/m ³	24-hour ⁽⁵⁾	Same as Primary	
Ozone	0.075 ppm (2008 std)	8-hour ⁽⁶⁾	Same as Primary	
	0.08 ppm (1997 std)	8-hour ⁽⁷⁾	Same as Primary	
	0.12 ppm	1-hour ⁽⁸⁾ (Applies only in limited areas)	Same as Primary	
Sulfur Dioxide	0.03 ppm	Annual (Arithmetic Mean)	0.5 ppm (1300 µg/m ³)	3-hour ⁽¹⁾
	0.14 ppm	24-hour ⁽¹⁾		

- (1) Not to be exceeded more than once per year.
- (2) Final rule signed October 15, 2008.
- (3) Not to be exceeded more than once per year on average over 3 years.
- (4) To attain this standard, the 3-year average of the weighted annual mean PM_{2.5} concentrations from single or multiple community-oriented monitors must not exceed 15 µg/m³.
- (5) To attain this standard, the 3-year average of the 98th percentile of 24-hour concentrations at each population-oriented monitor within an area must not exceed 35µg/m³ (effective December 17, 2006).
- (6) To attain this standard, 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 must not exceed 0.075 ppm (effective May 27, 2008).
- (7) (a) To attain this standard, 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 must not exceed 0.08 ppm.
(b) The 1997 standard – and the implementation rules for that standard – will remain in place for implementation purposes as EPA undertakes rulemaking to address the transition from the 1997 ozone standard to the 2008 ozone standard.
- (8) (a) The standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm is ≤ 1.
(b) As of June 15, 2005, EPA revoked the 1-hour ozone standard in all areas except the 8-hour ozone nonattainment Early Action Compact (EAC) Areas.

EPA data showing the number of people living in counties with pollutant concentrations above NAAQS levels during 2007 are shown in Figure 1-4. All counties were in compliance with the NAAQS for CO, NO_x, and SO₂. Significant fractions of the population were exposed to ozone and PM_{2.5} concentrations that exceeded the standard, while smaller numbers were exposed

to lead and PM₁₀ concentrations in excess of the standard. Much of the difficulty in reaching the ozone standard stems from the fact that ozone is a secondary pollutant. Direct emissions of ozone are negligible and control strategies must address ozone precursors, many of which are naturally occurring.

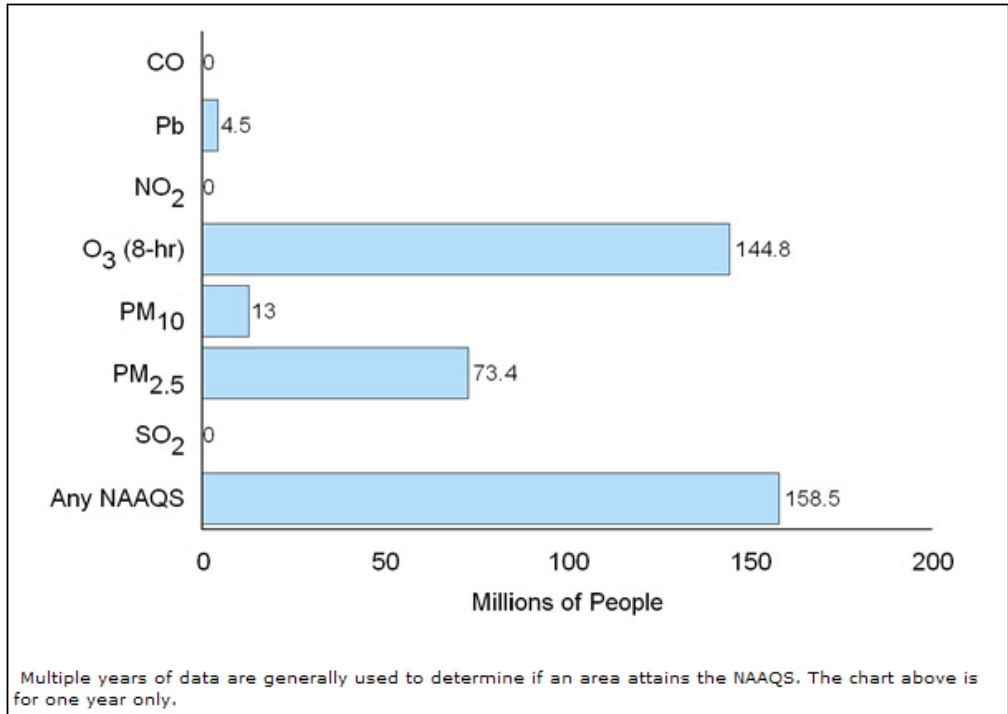


Figure 1-4. Number of people living in counties with air quality concentrations above the level of the NAAQS in 2007.

Review Exercises

1. What fraction of the sulfur present in a fossil fuel (i.e., coal, oil) is converted to sulfur dioxide in a utility or industrial boiler?
 - a. 25% to 30%
 - b. 50% to 75%
 - c. 75% to 90%
 - d. 94% to 95%
2. What factors influence the formation of NO_x in a boiler?
 - a. Temperature
 - b. Oxygen concentration
 - c. Fuel nitrogen content
 - d. All of the above
3. Which categories of air pollutants are responsible for the formation of photochemical smog? Select all that apply.
 - a. Volatile organic compounds
 - b. Nitrogen oxides
 - c. Sulfur dioxide
 - d. Carbon monoxide
4. Ozone is a _____ air pollutant.
 - a. primary
 - b. secondary
5. Which category of sources is most responsible for VOC emissions?
 - a. Transportation (automobiles, trucks, planes)
 - b. Fuel handling and distribution
 - c. Solvent utilization
 - d. Fuel combustion
6. Which category of sources is most responsible for sulfur dioxide emissions?
 - a. Utility and industrial boilers
 - b. Industrial processes
 - c. Transportation
 - d. None of the above

7. Which category of sources has the highest NO_x emissions?
 - a. Transportation (automobiles, trucks, planes)
 - b. Fuel handling and distribution
 - c. Solvent utilization
 - d. Fuel combustion (electric utilities)

8. When were National Ambient Air Quality Standards initiated for sulfur dioxide?
 - a. 1961
 - b. 1970
 - c. 1977
 - d. 1990

9. What type of regulation limits the emission of toxic pollutants?
 - a. New Source Performance Standards (NSPS)
 - b. National Ambient Air Quality Standards (NAAQS)
 - c. Maximum Achievable Control Technology Standards (MACTS)
 - d. Best Available Control Technology (BACT)

10. Why are VOC emissions controlled?
 - a. To achieve the ozone NAAQS
 - b. To achieve the hydrocarbon NAAQS
 - c. To achieve the NO_x NAAQS
 - d. To achieve the MACTs

Review Answers

1. What fraction of the sulfur present in a fossil fuel (i.e., coal, oil) is converted to sulfur dioxide in a utility or industrial boiler?
 - d. 94% to 95%
2. What factors influence the formation of NO_x in a boiler?
 - d. All of the above
3. Which categories of air pollutants are primarily responsible for the formation of photochemical smog? Select all that apply.
 - a. Volatile organic compounds
 - b. Nitrogen oxides
 - d. Carbon monoxide
4. Ozone is a _____ air pollutant.
 - b. secondary
5. Which category of sources is most responsible for VOC emissions?
 - c. Solvent utilization
6. Which category of sources is most responsible for sulfur dioxide emissions?
 - a. Utility and industrial boilers
7. Which category of sources has the highest NO_x emissions?
 - a. Transportation (automobiles, trucks, planes)
8. When were National Ambient Air Quality Standards initiated for sulfur dioxide?
 - b. 1970
9. What type of regulation limits the emission of toxic pollutants?
 - c. Maximum Achievable Control Technology Standards (MACTS)
10. Why are VOC emissions controlled?
 - a. To achieve the ozone NAAQS

References

1. *National Air Quality and Emissions Trend Report, 1997*; EPA 454/R-98-016; U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards: Research Triangle Park, NC, 1998.