# 10

# Sources of Air Pollution

## I. GENERAL

The sources of air pollution are nearly as numerous as the grains of sand. In fact, the grains of sand themselves are air pollutants when the wind entrains them and they become airborne. We would class them as a natural air pollutant, which implies that such pollution has always been with us. Natural sources of air pollution are defined as sources not caused by people in their activities.

Consider the case in which someone has removed the ground cover and left a layer of exposed soil. Later the wind picks up some of this soil and transports it a considerable distance to deposit it at another point, where it affects other people. Would this be classed as a natural pollutant or an anthropogenic pollutant? We might call it natural pollution if the time span between when the ground cover was removed and when the material became airborne was long enough. How long would be long enough? The answers to such questions are not as simple as they first appear. This is one of the reasons why pollution problems require careful study and analysis before a decision to control them at a certain level can be made.

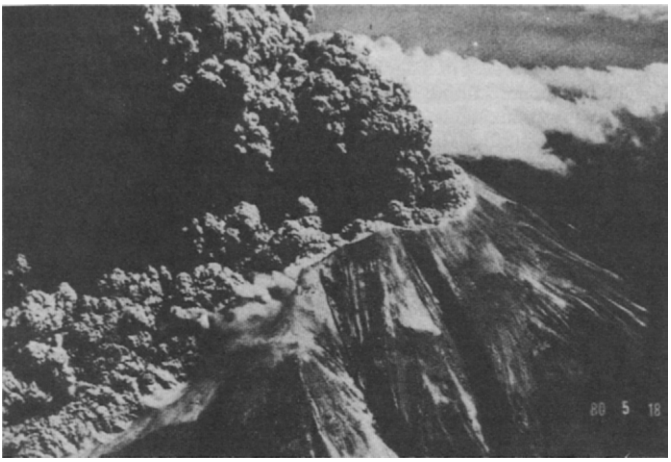


**Fig. 10.1.** Mt. St. Helens during the eruption on May 1980. *Source*: Photo by C. Rosenfeld, Oregon Air National Guard.

## A. Natural Sources

An erupting volcano emits particulate matter. Pollutant gases such as $SO_2$, $H_2S$, and methane are also emitted. The emission from an eruption may be of such magnitude as to harm the environment for a considerable distance from the volcanic source. Clouds of volcanic particulate matter and gases have remained airborne for very long periods of time. The eruption of Mt. St. Helens in the state of Washington is a classic example of volcanic activity. Figure 10.1 is a photograph of Mt. St. Helens during the destructive eruption on May 18, 1980.

Accidental fires in forests and on the prairies are usually classified as natural sources even though they may have been originally ignited by human activities. In many cases foresters intentionally set fires in forestlands to burn off the residue, but lightning setting off a fire in a large section of forestland could only be classed as natural. A large uncontrolled forest fire, as shown in Fig. 10.2, is a frightening thing to behold. Such a fire emits large quantities of pollutants in the form of smoke, unburned hydrocarbons, carbon monoxide, carbon dioxide, oxides of nitrogen, and ash. Forest fires in the Pacific Northwest of the United States have been observed to emit a plume which caused reduction in visibility and sunlight as far away as 350 km from the actual fire.

Dust storms that entrain large amounts of particulate matter are a common natural source of air pollution in many parts of the world. Even a relatively small dust storm can result in suspended particulate matter readings one or two orders of magnitude above ambient air quality standards. Visibility reduction during major dust storms is frequently the cause of severe highway accidents and can even affect air travel. The particulate matter transferred by dust storms from the desert to urban areas causes problems to householders, industry, and automobiles. The materials removed by the air cleaner of an

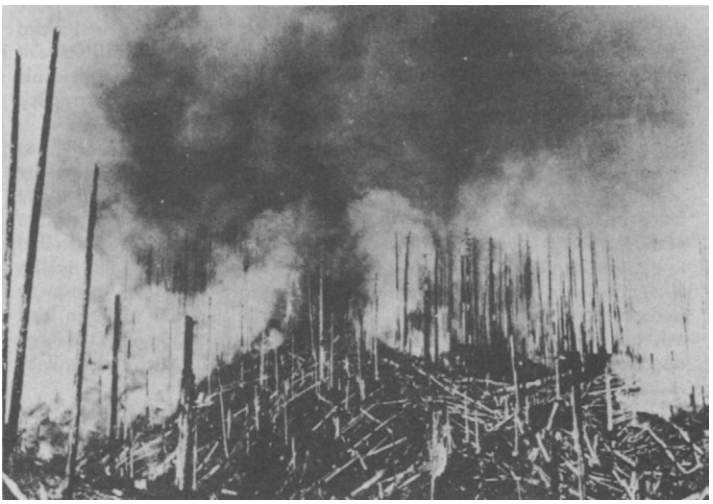

**Fig. 10.2.** Uncontrolled forest fire. *Source*: Information and Education Section, Oregon Department of Forestry.

automobile are primarily natural pollutants such as road dust and similar entrained material.

The oceans of the world are an important natural source of pollutant material. The ocean is continually emitting aerosols to the atmosphere, in the form of salt particles, which are corrosive to metals and paints. The action of waves on rocks reduces them to sand, which may eventually become airborne. Even the shells washed up on the beach are eroded by wave and tidal action until they are reduced to such a small size that they too may become airborne.

An extensive source of natural pollutants is the trees and other plant life of the earth. Even though these green plants play a large part in the conversion of carbon dioxide to oxygen through photosynthesis, they are still the major source of hydrocarbons on the planet. The familiar blue haze over forested areas is nearly all from the atmospheric reactions of the volatile organics given off by the trees of the forest [1]. Another air pollutant problem, which can be attributed to plant life, is the pollens which cause respiratory distress and allergic reactions in humans.

Other natural sources, such as alkaline and saltwater lakes, are usually quite local in their effect on the environment. Sulfurous gases from hot springs also fall into this category in that the odor is extremely strong when close to the source but disappears a few kilometers away.

## B. Anthropogenic Sources

### *1. Industrial Sources*

The reliance of modern people on industry to produce their needs has resulted in transfer of the pollution sources from the individual to industry.

A soap factory will probably not emit as much pollution as did the sum total of all the home soap-cooking kettles it replaces, but the factory is a source that all soap consumers can point to and demand that it be cleaned up.

A great deal of industrial pollution comes from manufacturing products from raw materials—(1) iron and steel from ore, (2) lumber from trees, (3) gasoline and other fuels from crude oil, and (4) stone from quarries. Each of these manufacturing processes produces a product, along with several waste products which we term pollutants. Often, part or all of the polluting material can be recovered and converted into a usable product.

Industrial pollution is also emitted by industries that convert products to other products—(1) automobile bodies from steel, (2) furniture from lumber, (3) paint from solids and solvents, and (4) asphaltic paving from rock and oil.

Industrial sources are stationary, and each emits relatively consistent qualities and quantities of pollutants. A paper mill, for example, will be in the same place tomorrow that it is today, emitting the same quantity of the same kinds of pollutants unless a major process change is made. Control of industrial sources can usually be accomplished by applying known technology. The most effective regulatory control is that which is applied uniformly within all segments of industries in a given region, e.g., "Emission from all asphalt plant dryers in this region shall not exceed 230 mg of particulate matter per standard dry cubic meter of air."

### 2. *Utilities*

The utilities in our modern society are so much a part of our lives that it is hard to imagine how we survived without them. An electric power plant generates electricity to heat and light our homes in addition to providing power for the personal computer, television, refrigerator, and the recharging of the batteries for the laptop, cell phone, PDA, MP3 player, and electric toothbrush. When our homes were heated with wood fires, home-made candles were used for light, there were no television or entertainment appliances, and food was stored in a cellar, the total of the air pollution generated by all the individual sources probably exceeded that of the modern generating stations supplying today's energy. It is easy for citizens to point out the utility as an air pollution source without connecting their own use of the power to the pollution from the utility. Figure 10.3 illustrates an electric power plant.

Utilities are in the business of converting energy from one form to another and transporting that energy. If a large steam generating plant, producing 2000 MW, burns a million kilograms per hour of 4% ash coal, it must somehow dispose of 40 000 kg of ash per hour. Some will be removed from the furnaces by the ash-handling systems, but some will go up the stack with the flue gases. If 50% of the ash enters the stack and the fly ash collection system is 99% efficient, 200 kg of ash per hour will be emitted to the atmosphere. For a typical generating plant, the gaseous emissions would include 341 000 kg of oxides of

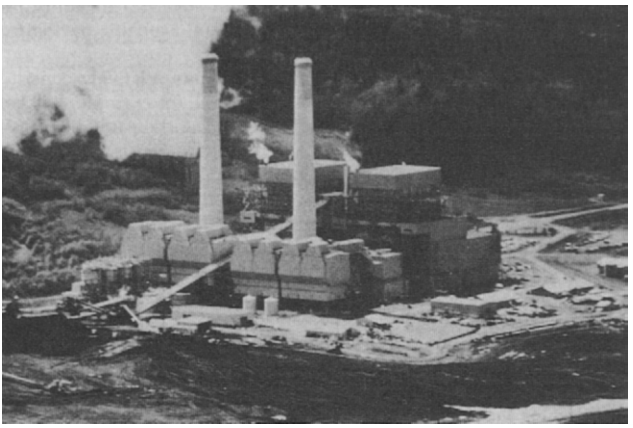

**Fig. 10.3.** Coal-fired electric generating plant.

sulfur per day and 185 000 kg of oxides of nitrogen per day. If this is judged as excessive pollution, the management decision can be to (1) purchase lower-ash or lower-sulfur coal, (2) change the furnace so that more ash goes to the ash pit and less goes up the stack, or (3) install more efficient air pollution control equipment. In any case, the cost of operation will be increased and this increase will be passed on to the consumer.

Another type of utility that is a serious air pollution source is the one that handles the wastes of modern society. An overloaded, poorly designed, or poorly operated sewage treatment plant can cause an air pollution problem which will arouse citizens to demand immediate action. In many countries around the world, open dumps still exist. These may catch fire and release harmful plumes of smoke and fumes. Even in more economically developed nations, landfills remain sources of dust and smoke, as are fires in abandoned mines shafts and in industrial waste disposal and reclamation sites. These are certainly sources of public complaint, even though it may be explained to the same public that it is the "cheapest" way to dispose of their solid waste. The public has shown its willingness to ban burning dumps and pay the additional cost of adequate waste disposal facilities to have a pollution-free environment.

### *3. Personal Sources*

Even though society has moved toward centralized industries and utilities, we still have many personal sources of air pollution for which we alone can answer—(1) automobiles, (2) home furnaces, (3) home fireplaces and stoves, (4) backyard barbecue grills, and (5) open burning of refuse and leaves. Figure 10.4 illustrates the personal emissions of a typical US family.

The energy release and air pollution emissions from personal sources in the United States are greater than those from industry and utilities combined.

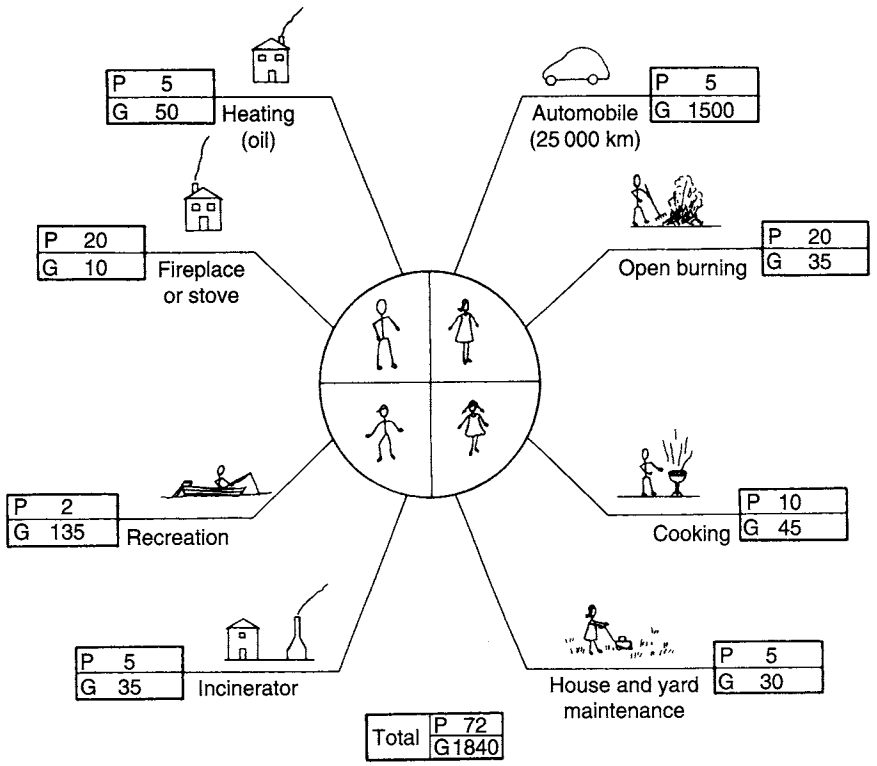


**Fig. 10.4.** Estimated personal emissions from US family of four persons. P, particulate matter in kilograms per year; G, gases in kilograms per year.

In any major city in the United States, the mass of pollutants emitted by the vast numbers of private automobiles exceeds that from any other source.

Control of these personal sources of pollution takes the form of (1) regulation (fireplaces and stoves may be used only when atmospheric mixing is favorable), (2) change of lifestyle (sell the automobile and ride public transportation), (3) change from a more polluting to a less polluting source (convert the furnace to natural gas), or (4) change the form of pollution (instead of burning leaves, haul them to the city landfill for composting). Whatever method is used for control of pollution from personal sources, it is usually difficult and unpopular to enforce. It is difficult to get citizens to believe that their new, highly advertised, shiny, unpaid-for automobiles are as serious a pollution problem as the smoking factory stack on the horizon. It is also a very ineffective argument to point out that the workers at that factory put more pollution into the air each day by driving their automobiles to and from work, or by mowing their lawns on Saturday, than does the factory with its visible plume of smoke.

## II. COMBUSTION

Combustion is the most widely used, and yet one of the least understood, chemical reactions at our disposal. *Combustion* is defined as the rapid union of a substance with oxygen accompanied by the evolution of light and heat [2].

The economies of highly industrialized nations are heavily dependent on combustion. Much of the transportation by automobile, rail, and airlines is based on internal combustion engines that burn gasoline or diesel fuels. Small internal combustion engines are deceivingly important sources of air pollutants. In fact, with the advent of low emitting vehicles (LEVs), lawn mower usage for 1 h emits about as much as driving a car 100 miles (650 miles for a vehicle made before 1990). A push mower emits as much hourly pollution as 11 cars and a riding mower emits as much as 34 cars. Since small engine use exceeds three billion hours per year in the United States, the US EPA proposed a rule in 2007 to reduce small engine exhaust of hydrocarbons by 35% and oxides of nitrogen emissions by 60%. In addition, fuel evaporative emissions of hydrocarbons are expected to fall by 45% if the rule is implemented. To meet exhaust emission standards, manufacturers are expected to use catalytic converters for the first time in numerous small watercraft, lawn, and garden equipment. The rule also lays out fuel evaporative standards, national standards for vessels powered by sterndrive or inboard engines, and CO standards for gasoline-powered engines used in recreational watercraft [3]. Combustion is the relatively simple phenomenon of oxidizing a substance in the presence of heat. Chemically, efficient combustion is

$$(CH)_x + O_2 \rightarrow CO_2 + H_2O \tag{10.1}$$

Most thermal processes, however, do not reach complete combustion. More complex combustion reactions are shown in Table 10.1. They are usually oxygen limited, leading to the generation of a wide variety of compounds, many that are toxic. Other reactions besides combustion also produce air pollutants. Decomposition of a substance in the absence of oxygen is known as pyrolysis. In fact, a single fire can have pockets of both combustion and pyrolytic processes. This lack of homogeneity results in temperatures varying in both space and time. Plastic fires, for example, can release over 450 different organic compounds.[1] The relative amount of combustion and pyrolysis in a fire affects the actual amounts and types of compounds released.

Temperature is also important, but there is no direct relationship between temperature and pollutants released. For example, Fig. 10.5 shows that in a

[1] Levin, B.C., A summary of the NBS literature reviews on the chemical nature and toxicity of pyrolysis and combustion products from seven plastics: acrylonitrile–butadiene–styrenes; nylons; polyesters; polyethylenes; polystyrenes; poly(vinyl chlorides) and rigid polyurethane foams. *Fire Mater.* **11**, 143–157 (1987).

TABLE 10.1

**Balanced Combustion Reactions for Selected Organic Compounds**

| | |
|---|---|
| Chlorobenzene | $C_6H_5Cl + 7O_2 \rightarrow 6CO_2 + HCl + 2H_2O$ |
| Tetrachloroethene (TCE) | $C_2Cl_4 + O_2 + 2H_2O \rightarrow 2CO_2 + HCl$ |
| Hexachloroethane (HCE) | $C_2Cl_6 + \frac{1}{2}O_2 + 3H_2O \rightarrow 2CO_2 + 6HCl$ |
| Post-chlorinated polyvinyl chloride (CPVC) | $C_4H_5Cl_3 + 4\frac{1}{2}O_2 \rightarrow 4CO_2 = 3HCl + H_2O$ |
| Natural gas fuel (methane) | $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ |
| PTEE Teflon | $C_2F_4 + O_2 \rightarrow CO_2 + 4HF$ |
| Butyl rubber | $C_9H_{16} + 13O_2 \rightarrow 9CO_2 + 8H_2O$ |
| Polyethylene | $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$ |

Wood is considered to have the composition of $C_{6.9}H_{10.6}O_{3.5}$. Therefore, the combustion reactions are simple carbon and hydrogen combustion:

$$C + O_2 \rightarrow CO_2$$
$$H + 0.25O_2 \rightarrow 0.5H_2O$$

*Source*: US Environmental Protection Agency

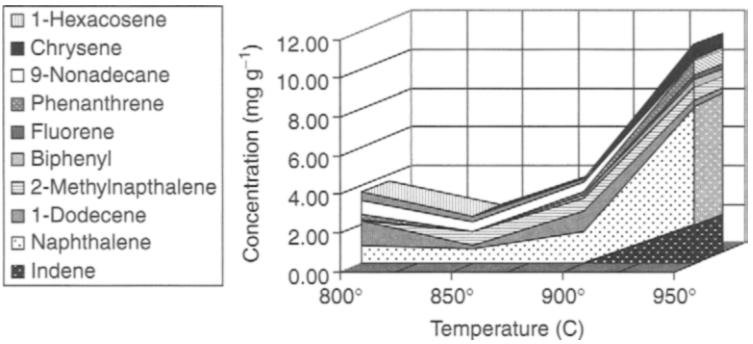


**Fig. 10.5.** Selected hydrocarbon compounds generated in a low-density polyethylene fire (pyrolysis) in four temperature regions. Data from Hawley-Fedder, R. A., Parsons, M. L., and Karasek, F. W., Products obtained during combustion of polymers under simulated incinerator conditions. *J. Chromatogr.* **314**, 263–272 (1984).

plastics fire (i.e. low-density polyethylene pyrolysis) compounds are generated at lower temperatures, but for others the optimal range is at higher temperatures. The aliphatic compounds in this fire (i.e. 1-dodecene, 9-nonadecane, and 1-hexacosene) are generated in higher concentrations at lower temperatures (about 800°C), and the aromatics need higher temperatures (see Figs. 10.5 and 10.6).

We use combustion primarily for heat by changing the potential chemical energy of the fuel to thermal energy. We do this in a fossil fuel-fired power plant, a home furnace, or an automobile engine. We also use combustion as a means of destruction for our unwanted materials. We reduce the volume of

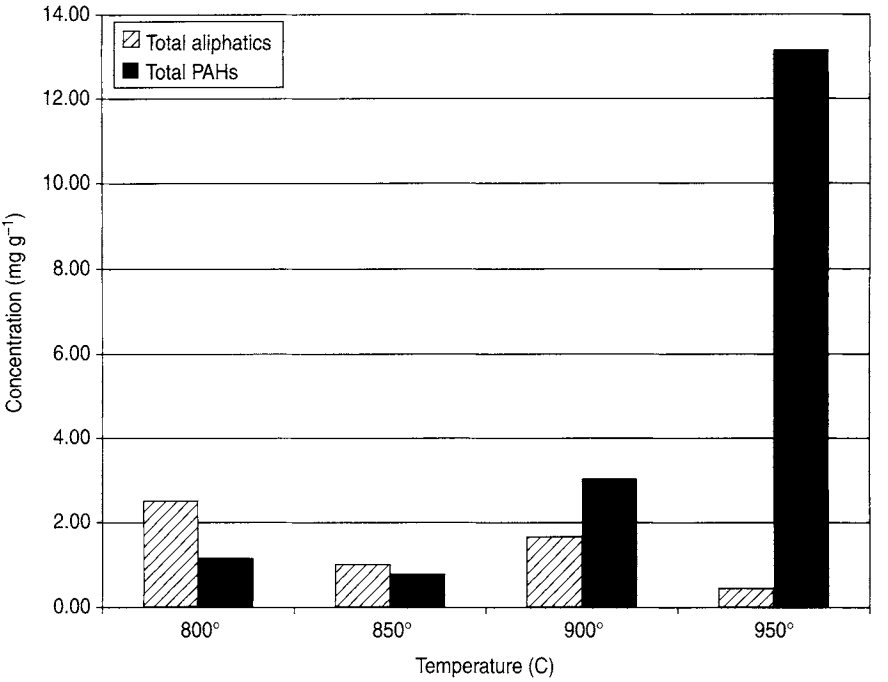


**Fig. 10.6.** Total aliphatic (chain) hydrocarbons versus polycyclic aromatic hydrocarbons (PAHs) generated in a low-density polyethylene fire (pyrolysis) in four temperature regions. Data from: Hawley-Fedder, R. A., Parsons, M. L., and Karasek, F. W., Products obtained during combustion of polymers under simulated incinerator conditions. *J. Chromatogr.* **314**, 263–272, 1984.

a solid waste by burning the combustibles in an incinerator. We subject combustible gases, with undesirable properties such as odors, to a high temperature in an afterburner system to convert them to less objectionable gases.

The efficient reaction can be seen as two combustion equations that are simple:

$$C + O_2 \rightarrow CO_2 \tag{10.2}$$

$$2H_2 + O_2 \rightarrow 2H_2O \tag{10.3}$$

They produce the products carbon dioxide and water, which are odorless and invisible.

The problems with the combustion reaction occur because the process also produces many other products, most of which are termed as *air pollutants*. These can be carbon monoxide, carbon dioxide, oxides of sulfur, oxides of nitrogen, smoke, fly ash, metals, metal oxides, metal salts, aldehydes, ketones, acids, polycyclic aromatic hydrocarbons (PAHs), hexachlorobenzene, dioxins, furans, volatile organic compounds (VOCs), and many others. Only in the past few decades have combustion engineers become concerned about

these relatively small quantities of materials emitted from the combustion process. An automotive engineer, for example, was not overly concerned about the 1% of carbon monoxide in the exhaust of the gasoline engine. By getting this 1% to burn to carbon dioxide inside the combustion chamber, the engineer could expect an increase in gasoline mileage of something less than one-half of 1%. This 1% of carbon monoxide, however, is 10 000 ppm by volume, and a number of such magnitudes cannot be ignored by an engineer dealing with air pollution problems.

Combustion is extremely complicated but is generally considered to be a free radical chain reaction. Several reasons exist to support the free radical mechanism: (1) Simple calculations of the heats of disassociation and formation for the molecules involved do not agree with the experimental values obtained for heats of combustion. (2) A great variety of end products may be found in the exhaust from a combustion reaction. Many complicated organic molecules have been identified in the effluent from a system burning pure methane with pure oxygen. (3) Inhibitors, such as tetraethyl lead and methylcyclopentadienyl manganese tricarbonyl (MMT)[2], can greatly change the rate of reaction [3].

When visualizing a combustion process, it is useful to think of it in terms of the three Ts: time, temperature, and turbulence. Time for combustion to occur is necessary. A combustion process that is just initiated, and suddenly has its reactants discharged to a chilled environment, will not go to completion and will emit excessive pollutants. A high enough temperature must exist for the combustion reaction to be initiated. Combustion is an exothermic reaction (it gives off heat), but it also requires energy to be initiated. This is illustrated in Fig. 10.7.

[2] MMT $(CH_3C_5H_4)Mn(CO)_3$ is an octane enhancer, which was approved as a fuel additive in the US. Some decades ago, the US EPA determined that MMT, added at 1/32 grams per gallon of manganese (Mn), will not cause or contribute to regulated emissions failures of vehicles. Some have expressed concerns that the use of MMT may harm on-board diagnostic equipment (OBD) which monitors the performance of emissions control devices in the vehicle. Currently, the Agency believes the data collected is inconclusive with regard to OBD. After completing a 1994 risk evaluation on the use of MMT in gasoline, the US EPA was unable to determine if there is a risk to the public health from exposure to emissions of MMT gasoline. Like lead, manganese is also neurotoxic, so the US EPA has required the manufacturer perform testing to support a more definitive risk evaluation, including health pharmacokinetic (PK) studies and one emission characterization. Completed final reports for all of these studies have been submitted to EPA. These final reports can be found in the Federal Docket Management System (FDMS) at www.regulations.gov identified by docket number EPA-HQ-OAR-2004-0074. In addition to the already completed tests, the manufacturer is now in the process of developing physiologically based pharmacokinetic (PBPK) models for manganese which are being derived from data generated from the completed testing. The manufacturer anticipates that these PBPK models will be completed in 2008. The US EPA is presently reviewing exposure and risk information and may refine its risk evaluation or may ask for further testing based on the results of the submitted testing and resulting model now being developed, as well as any other available data. See http://www.epa.gov/otaq/regs/fuels/additive/mmt_cmts.htm.

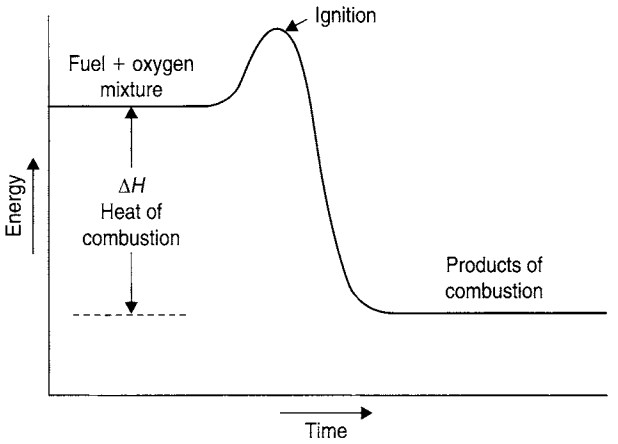


**Fig. 10.7.** Energies involved in combustion processes.

Turbulence is necessary to ensure that the reacting fuel and oxygen molecules in the combustion process are in intimate contact at the proper instant, when the temperature is high enough to cause the reaction to begin.

The physical state of the fuel for a combustion process dictates the type of system to be used for burning. A fuel may be composed of volatile material, fixed carbon, or both. The volatile material burns as a gas and exhibits a visible flame, whereas the fixed carbon burns without a visible flame in a solid form. If a fuel is in the gaseous state, such as natural gas, it is very reactive and can be fired with a simple burner.

If a fuel is in the liquid state, such as fuel oil, most of it must be vaporized to the gaseous state before combustion occurs. This vaporization can be accomplished by supplying heat from an outside source, but usually the liquid fuel is first atomized and then the finely divided fuel particles are sprayed into a hot combustion chamber to accomplish the gasification.

With a solid fuel, such as coal or wood, a series of steps are involved in combustion. These steps occur in a definite order, and the combustion device must be designed with these steps in mind. Figure 10.8 shows what happens to a typical solid fuel during the combustion process.

The cycle of operation of the combustion source is very important as far as emissions are concerned. A steady process, such as a large steam boiler, operates with a fairly uniform load and a continuous fuel flow. The effluent gases, along with any air pollutants, are discharged steadily and continually from the stack. An automobile engine, on the other hand, is a series of intermittent sources. The emissions from the automotive engine will be vastly different from those from the boiler in terms of both quantity and quality. A four-cylinder automotive engine operating at 2500 rpm has 5000 separate combustion processes started and completed each minute of its operation. Each of these lasts about 1/100 of a second from beginning to end.

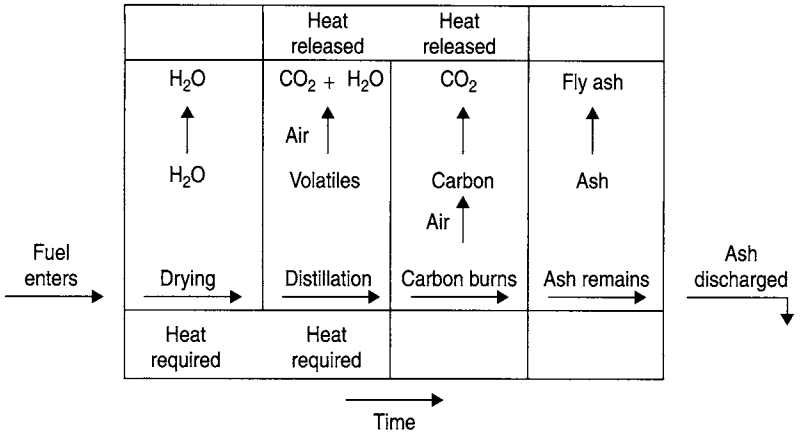


**Fig. 10.8.** Solid fuel combustion schematic.

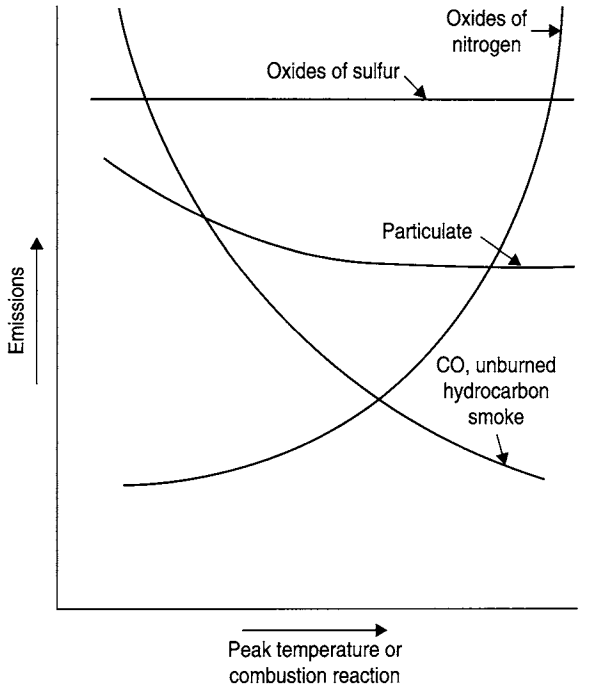


**Fig. 10.9.** Combustion emissions as a function of peak combustion temperatures.

The emissions from combustion processes may be predicted to some extent if the variables of the processes are completely defined. Figure 10.9 indicates how the emissions from a combustion source would be expected to vary with the temperature of the reaction. No absolute values are shown, as these will vary greatly with fuel type, independent variables of the combustion process, etc.

TABLE 10.2

**Comparison of Combustion Pollutants**[a]

| Contaminant | Power plant emission ($gm\,kg^{-1}$ fuel) | | | Refuse burning emission ($gm\,kg^{-1}$ refuse) | | Uncontrolled automotive emission ($gm\,kg^{-1}$ fuel) | |
|---|---|---|---|---|---|---|---|
| | Coal | Oil | Gas | Open burning | Multiple chamber | Gasoline | Diesel |
| Carbon monoxide | Nil | Nil | Nil | 50.0 | Nil | 165.0 | Nil |
| Oxides of sulfur ($SO_2$) | $(20)x$ | $(20)x$ | $(16)x$ | 1.5 | 1.0 | 0.8 | 7.5 |
| Oxides of nitrogen ($NO_2$) | 0.43 | 0.68 | 0.16 | 2.0 | 1.0 | 16.5 | 16.5 |
| Aldehydes and ketones | Nil | 0.003 | 0.001 | 3.0 | 0.5 | 0.8 | 1.6 |
| Total hydrocarbons | 0.43 | 0.05 | 0.005 | 7.5 | 0.5 | 33.0 | 30.0 |
| Total particulate | $(75)y$ | $(2.8)y$ | Nil | 11 | 11 | 0.05 | 18.0 |

[a] $x$ = percentage of sulfur in fuel; $y$ = percentage of ash in fuel.

A comparison of typical emissions from various common combustion sources may be seen in Table 10.2.

## III. STATIONARY SOURCES

Emissions from industrial processes are varied and often complex [4]. These emissions can be controlled by applying the best available technology. The emissions may vary slightly from one facility to another, using apparently similar equipment and processes, but in spite of this slight variation, similar control technology is usually applied [5]. For example, a method used to control the emissions from steel mill X may be applied to control similar emissions at plant Y. It should not be necessary for plant Y to spend excessive amounts for research and development if plant X has a system that is operating satisfactorily. The solution to the problem is often to look for a similar industrial process, with similar emissions, and find the type of control system used. That said, good engineering must always consider the details in any design. Thus, even seemingly small differences between two similar processes (e.g. quantity, flow rates, holding times, materials and reactor size and shape) can lead to dramatically different waste products, not to mention unforeseen safety and liability issues. Consequently, the following discussions are merely guidelines that must be adapted for each facility.

### A. Chemical and Allied Products

The emissions from a chemical process can be related to the specific process. A plant manufacturing a resin might be expected to emit not only the resin being manufactured but also some of the raw material and some other

products which may or may not resemble the resin. A plant manufacturing sulfuric acid can be expected to emit sulfuric acid fumes and $SO_2$. A plant manufacturing soap products could be expected to emit a variety of odors. Depending on the process, the emissions could be any one or a combination of dust, aerosols, fumes, or gases. The emissions may or may not be odorous or toxic. Some of the primary emissions might be innocuous but later react in the atmosphere to form an undesirable secondary pollutant. A flowchart and material balance sheet for the particular process are very helpful in understanding and analyzing any process and its emissions [6].

In any discussion of the importance of emissions from a particular process for an area, several factors must be considered—(1) the percentage of the total emissions of the area that the particular process emits, (2) the degree of toxicity of the emissions, and (3) the obvious characteristics of the source (which can be related to either sight or smell).

### B. Resins and Plastics

Resins are solid or semisolid, water-insoluble,[3] organic substances with little or no tendency to crystallize. They are the basic components of plastics and are also used for coatings on paper, particleboard, and other surfaces that require a decorative, protective, or special-purpose finish. The common characteristic of resins is that heat is used in their manufacture and application, and gases are exhausted from these processes. Some of the gases that are economically recoverable may be condensed, but a large portion is lost to the atmosphere. One operation, coating a porous paper with a resin to form battery separators, was emitting to the atmosphere about 85% of the resin purchased. This resin left the stacks of the plant as a blue haze, and the odor was routinely detected more than 2 km away. Since most resins and their by-products have low-odor thresholds, disagreeable odor is the most common complaint against any operation using them.

### C. Varnish and Paints

In the manufacture of varnish, heat is necessary for formulation and purification. The same may be true of operations preparing paints, shellac, inks, and other protective or decorative coatings. The compounds emitted to the atmosphere are gases, some with extremely low-odor thresholds. Acrolein, with an odor threshold of about $4000\,\mu g\,m^{-3}$, and reduced sulfur compounds, with odor thresholds of $2\,\mu g\,m^{-3}$, are both possible emissions from varnish cooking operations. The atmospheric emissions from varnish cooking appear

[3] However, the reactants and other materials used to produce or modify resins and plastics (e.g. polymers) may include chemicals with high aqueous solubility, such as the neurotoxic compound, acrylamide ($650\,000\,mg\,L^{-1}$). This means that such ancillary chemicals can find their way to the air via water vapor or water films on particles. They may also move to other environmental compartments (e.g. contaminating surface and ground water).

to have little or no recovery value, whereas some of the solvents used in paint preparation are routinely condensed for recovery and returned to the process. If a paint finish is baked to harden the surface by removal of organic solvents, the solvents must either be recovered, destroyed, or emitted to the atmosphere. The last course, emission to the atmosphere, is undesirable and may be prohibited by the air pollution control agency.

## D. Acid Manufacture

Acids are used as basic raw materials for many chemical processes and manufacturing operations. Figure 10.10 illustrates an acid plant with its flow diagram. Sulfuric acid is one of the major inorganic chemicals in modern industry. The atmospheric discharges from a sulfuric acid plant can be expected to contain gases including $SO_2$ and aerosol mists, containing $SO_3$ and $H_2SO_4$, in the submicron to 10-μm size range. The aerosol mists are particularly damaging to paint, vegetation, metal, and synthetic fibers.

Other processes producing acids, such as nitric, acetic, and phosphoric acids, can be expected to produce acid mists from the processes themselves as well as various toxic and nontoxic gases. The particular process must be thoroughly studied to obtain a complete listing of all the specific emissions.

## E. Soaps and Detergents

Soaps are made by reacting fats or oils with a base. Soaps are produced in a number of grades and types. They may be liquid, solid, granules, or powder. The air pollution problems of soap manufacture are primarily odors from the chemicals, greases, fats, and oils, although particulate emissions may

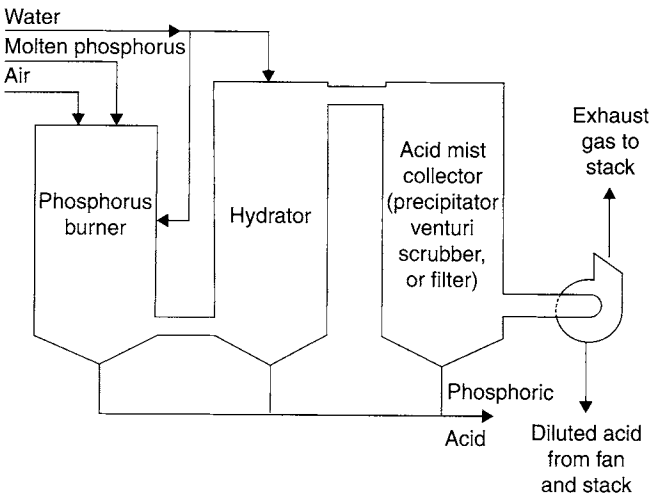


**Fig. 10.10.** Flow diagram for a phosphoric acid plant.

occur during drying and handling operations. Detergents are manufactured from base stocks similar to those used in petroleum refineries, so the air pollution problems are similar to those of refineries.

## F. Phosphate Fertilizers

Phosphate fertilizers are prepared by beneficiation of phosphate rock to remove its impurities, followed by drying and grinding. The $PO_4$ in the rock may then be reacted with sulfuric acid to produce normal superphosphate fertilizer. Over 100 plants operating in the United States produce approximately a billion kilograms of phosphate fertilizer per year. Figure 10.11 is a flow diagram for a normal superphosphate plant which notes the pollutants emitted. The particulate and gaseous fluoride emissions cause greatest concern near phosphate fertilizer plants.

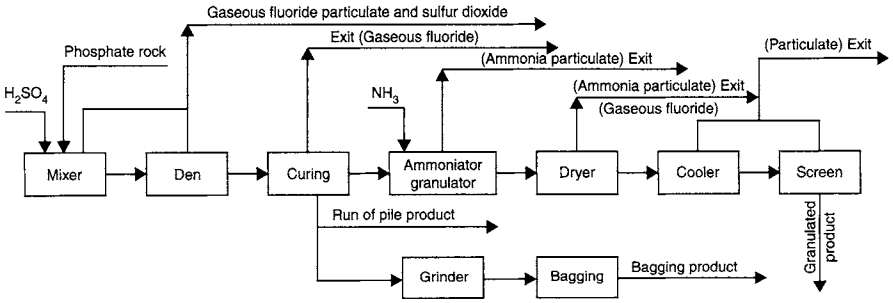


**Fig. 10.11.** Flow diagram for a normal superphosphate plant.

## G. Other Inorganic Chemicals

Production of the large quantities of inorganic chemicals necessary for modern industrial processes can result in air pollutant emissions as undesirable by-products. Table 10.3 lists some of the more common inorganic chemicals produced, along with the associated air pollutants potentially emitted from the specific process [6].

**TABLE 10.3**

**Miscellaneous Inorganic Chemicals and Associated Air Pollution Emissions**

| Inorganic chemical produced | Associated air pollution emissions |
|---|---|
| Calcium oxide (lime) | Lime dust |
| Sodium carbonate (soda ash) | Ammonia—soda ash dust |
| Sodium hydroxide (caustic soda) | Ammonia—caustic dust and mist |
| Ammonium nitrate | Ammonia—nitric oxides |
| Chlorine | Chlorine gas, hydrochloric acid (HCl) |
| Bromine | Bromine gas and compounds, chlorine gas, radionuclides |

## H. Petroleum and Coal

Petroleum and coal supply the majority of the energy in all industrial countries. This fact gives an indication of the vast quantities of materials handled and also hints at the magnitude of the air pollution problems associated with obtaining the resource, transporting it, refining it, and transporting it again. The emission problems from burning fossil fuel have been previously discussed.

### *1. Petroleum*

Petroleum products are obtained from crude oil. In the process of getting the crude oil from the ground to the refinery, many possibilities for emission of hydrocarbon and reduced sulfur gaseous emissions occur. In many cases, these operations take place in relatively remote regions and affect only those employed by the industry, so that little or no control is attempted.

As shown in Fig. 10.12, an uncontrolled petroleum refinery is a potential source of large tonnages of atmospheric emissions. All refineries are odorous, the degree being a matter of the housekeeping practices around the refinery. Since refineries are essentially closed processes, emissions are not normally considered a part of the operation. Refineries do need pressure relief systems and vents, and emissions from them are possible. Most refineries use very strict control measures for economic as well as regulatory reasons. The recovery of 1% or 2% of a refinery throughput which was previously lost to the atmosphere can easily pay for the cost of the control equipment. The expense of the catalyst charge in some crackers and regenerators requires that the best possible control equipment be used to prevent catalyst emissions to the atmosphere.

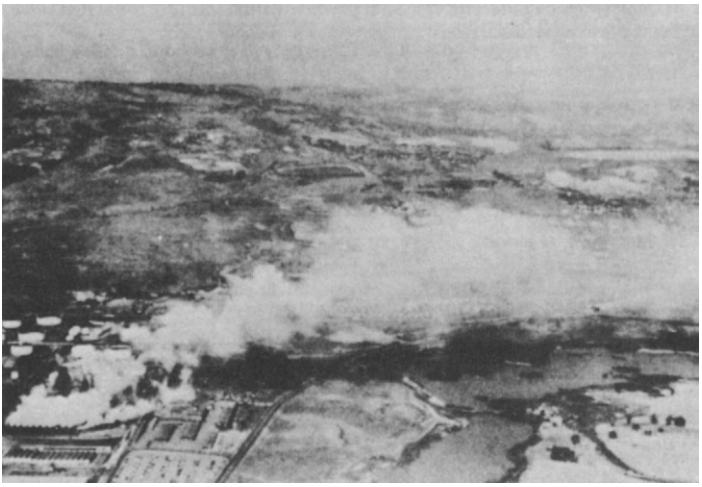

**Fig. 10.12.** Uncontrolled petroleum refinery.

Potential air pollutants from a petroleum refinery could include: (1) hydrocarbons from all systems, leaks, loading, and sampling; (2) sulfur oxides from boilers, treaters, and regenerators; (3) carbon monoxide from regenerators and incinerators; (4) nitrogen oxides from combustion sources and regenerators; (5) odors from air and steam blowing, condensers, drains, and vessels; and (6) particulate matter from boilers, crackers, regenerators, coking, and incinerators.

Loading facilities must be designed to recover all vapors generated during filling of tank trucks or tanker ships. Otherwise these vapors will be lost to the atmosphere. Since they may be both odorous and photochemically reactive, serious air pollution problems could result. The collected vapors must be returned to the process or disposed of by some means.

An increasingly important concern is the likelihood of an uncontrolled fire caused by an accident or by a terrorist act at the refinery. This can be the source of large and highly toxic plumes. Thus, refineries need special measures for protection and security, coupled with vigorously diligent monitoring, operation, and maintenance. Every refinery also needs an up-to-date contingency plan.

*2. Coal*

The air pollution problems associated with combustion of coal are of major concern. These problems generally occur away from the coal mine. The problems of atmospheric emissions due to mining, cleaning, handling, and transportation of coal from the mine to the user are of lesser significance as far as the overall air pollution problems are concerned. Whenever coal is handled, particulate emission becomes a problem. The emissions can be either coal dust or inorganic inclusions. Control of these emissions can be relatively expensive if the coal storage and transfer facilities are located near residential areas. This is particularly problematic in developing nations. For example, China's economic and industrial expansion over the past decade has been largely supported by coal combustion (about two-thirds of energy use). This leads to three types of problems:

1. Coal is among the worst fuels in terms of production of greenhouse gases, mainly $CO_2$.
2. Coal often has high sulfur and ash content, so it is a major source of oxides of sulfur and particulate matter, respectively.
3. Coal contains heavy metals, particularly mercury, so it is also a major contributor to air toxics.

## I. Primary Metals Industry

Metallurgical equipment has long been an obvious source of air pollution. The effluents from metallurgical furnaces are submicron-size dusts and fumes and hence are highly visible. The emissions from associated coke ovens are not only visible but odorous as well.

### 1. *Ferrous Metals*

Iron and steel industries have been concerned with emissions from their furnaces and cupolas since the industry started. Pressures for control have forced the companies to such a low level of permissible emissions that some of the older operations have been closed rather than spend the money to comply. Most of the companies controlling these operations have not gone out of business but rather have opened a new, controlled plant to replace each old plant. Table 10.4 illustrates the changes in the steelmaking processes that have occurred in the United States.

Air-polluting emissions from steelmaking furnaces include metal oxides, smoke, fumes, and dusts to make up the visible aerosol plume. They may also include gases, both organic and inorganic. If steel scrap is melted, the charge may contain appreciable amounts of oil, grease, and other combustibles that further add to the organic gas and smoke loadings. If the ore used has appreciable fluoride concentrations, the emission of both gaseous and particulate fluorides can be a serious problem.

Emissions from foundry cupolas are relatively small but still significant, in some areas. An uncontrolled 2-m cupola can be expected to emit up to 50 kg of dust, fumes, smoke, and oil vapor per hour. Carbon monoxide, oxides of nitrogen, and organic gases may also be expected. Control is possible, but the cost of the control may be prohibitive for the small foundry which only has one or two heats per week.

Steel-making is commonly associated with coke ovens. Coke is coal that has undergone pyrolysis, i.e. heated up to 1000–1400°C in the absence of oxygen, so it is not burned. This process intentionally releases gaseous components of the coal to produce nearly pure carbon [7].

Coke oven emissions are complex mixtures of gas, liquid, and solid phases, usually including a range of about 40 PAHs, as well as other products of incomplete combustion; notably formaldehyde, acrolein, aliphatic aldehydes, ammonia, carbon monoxide, nitrogen oxides, phenol, cadmium, arsenic, and

**TABLE 10.4**

**Changes in Steel-making Processes in the United States**

| | Production by specific process (%) | | | | |
|---|---|---|---|---|---|
| Year | Bessemer | Open hearth | Electric | Basic oxygen furnace | Total |
| 1920 | 21 | 78 | 1 | 0 | 100 |
| 1940 | 6 | 92 | 2 | 0 | 100 |
| 1960 | 2 | 89 | 7 | 2 | 100 |
| 1970 | 1 | 36 | 14 | 48 | 100 |
| 1980 | 1 | 22 | 31 | 46 | 100 |
| 1990 | 0 | 4 | 37 | 59 | 100 |

mercury. More than 60 organic compounds have been collected near coke plants. A metric ton of coal yields up to 635 kg of coke, up to 90 kg of coke breeze (large coke particulates), 7–9 kg of ammonium sulfate, 27.5–34 L of coke oven gas tar, 55–135 L of ammonia liquor, and 8–12.5 L of light oil. Up to 35% of the initial coal charge is emitted as gases and vapors. Most of these gases and vapors are collected during by-product coke production. Coke oven gas is comprised of hydrogen, methane, ethane, carbon monoxide, carbon dioxide, ethylene, propylene, butylene, acetylene, hydrogen sulfide, ammonia, oxygen, and nitrogen. Coke oven gas tar includes pyridine, tar acids, naphthalene, creosote oil, and coal-tar pitch. Benzene, xylene, toluene, and solvent naphthas may be extracted from the light oil fraction. Coke production in the US increased steadily between 1880 and the early 1950s, peaking at 65 million metric tons in 1951. In 1976, the United States was second in the world with 48 million metric tons of coke, i.e. 14.4% of the world production. By 1990, the US produced 24 million metric tons, falling to fourth in the world. A gradual decline in production has continued; production has decreased from 20 million metric tons in 1997 to 15.2 million metric tons in 2002. Demand for blast furnace coke also has declined in recent years because technological improvements have reduced the amount of coke consumed per amount of steel produced by as much as 25%.

Obviously, the volatilized gases are air pollutants. In fact, coke ovens are the source of thousands of compounds, many that are toxic. Coke facilities have recognized that many of these gases are also economically valuable, so technologies exist and are being applied to recover, separate, and sell them for profit. Some of the processes shown in Table 10.4 no longer need coke to produce steel. This is an example of green engineering.

*2. Nonferrous Metals*

Around the turn of the century, one of the most obvious effects of industry on the environment was the complete destruction of vegetation downwind from copper, lead, and zinc smelters. This problem was caused by the smelting of the metallic sulfide ores. As the metal was released in the smelting process, huge quantities of sulfur were oxidized to $SO_2$, which was toxic to much of the vegetation fumigated by the plume. Present smelting systems go to great expense to prevent the uncontrolled release of $SO_2$, but in many areas the recovery of the ecosystem will take years and possibly centuries.

Early aluminum reduction plants were responsible for air pollution because of the fluoride emissions from their operations. Fluoride emissions can cause severe damage to vegetation and to animals feeding on such vegetation. The end result was an area surrounding the plant devoid of vegetation. Such scenes are reminiscent of those downwind from some of the uncontrolled copper smelters. New aluminum reduction plants are going to considerable expense to control fluoride emissions. Some of the older plants are finding that the cost of control will exceed the original capital investment in the entire facility. Where the problem is serious, control agencies have developed

extensive sampling networks to monitor emissions from the plant of concern.

Emissions from other nonferrous metal facilities are primarily metal fumes or metal oxides of extremely small diameter. Zinc oxide fumes vary from 0.03 to 0.3 μm and are toxic. Lead and lead oxide fumes are extremely toxic and have been extensively studied. Arsenic, cadmium, bismuth, and other trace metals can be emitted from many metallurgical processes.

## J. Stone and Clay Products

The industries which produce and handle various stone products emit considerable amounts of particulate matter at every stage of the operation. These particulates may include fine mineral dusts of a size to cause damage to the lungs. Depending on the type of rock, mineral fibers can also be released, notably asbestos. The threshold values for such dusts have been set quite low to prevent disabling diseases for the worker, including lung cancer, mesothelioma, pleural diseases, asbestosis, and silicosis.

In the production of clay, talc, cement, chalk, etc., an emission of particulate matter will usually accompany each process. These processes may involve grinding, drying, and sieving, which can be enclosed and controlled to prevent the emission of particles. In many cases, the recovered particles can be returned to the process for a net economic gain.

During the manufacture of glass, considerable dust, with particles averaging about 300 μm in size, will be emitted. Some dusts may also be emitted from the handling of the raw materials involved. Control of this dust to prevent a nuisance problem outside the plant is a necessity. When glass is blown or formed into the finished product, smoke and gases can be released from the contact of the molten glass with lubricated molds. These emissions are quite dense but of a relatively short duration.

## K. Forest Products Industry

### *1. Wood Processing*

Trees are classified as a renewable resource which is being utilized in most portions of the world on a sustained yield basis. A properly managed forest will produce wood for lumber, fiber, and chemicals indefinitely. Harvesting this resource can generate considerable dust and other particulates. Transportation over unpaved roads causes excessive dust generation. The cultural practice of burning the residue left after a timber harvest, called *slash burning*, is still practiced in some areas and is a major source of smoke, gaseous, and particulate air pollution in the localities downwind from the fire (see Fig. 10.13). Visibility reduction from such burning can be a serious problem.

Processing the harvested timber into the finished product may involve sawing, peeling, planing, sanding, and drying operations, which can release considerable amounts of wood fiber and lesser amounts of gaseous material to the

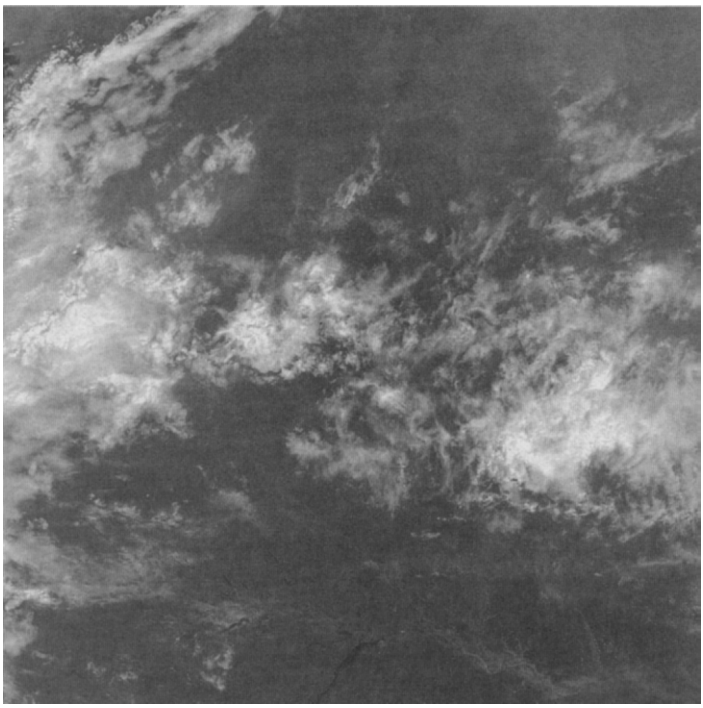

**Fig. 10.13.** Plume from slash burning in the Amazon region of South America. From the rainforests around the Amazon River (top) in Brazil, through the central highlands and into Bolivia to the southwest, numerous fires were burning throughout the region on September 8, 2002. The fires were detected by the Moderate Resolution Imaging Spectroradiometer (MODIS) on NASA's Terra satellite, and their locations are marked with red dots in this true-color image. Thick smoke and clouds are shrouding the highlands in the southern portion of the image. *Source*: Photo by J. Allen, based on data from the National Aeronautics and Space Administration, 2005, Goddard Space Flight, Space Visualization Studio, Maryland.

atmosphere. Control of wood fiber emissions from the pneumatic transport and storage systems can be a major problem of considerable expense for a plywood mill or a particleboard plant.

### 2. *Pulp and Paper*

Pulp and paper manufacture is increasing in the world at an exponential rate. The demand for paper will continue as new uses are found for this product. Since most paper is manufactured from wood or wood residue, it provides an excellent use for this renewable resource.

The most widely used pulping process is the kraft process, as shown in Fig. 10.14, which results in recovery and regeneration of the chemicals. This occurs in the recovery furnace, which operates with both oxidizing and reducing zones. Emissions from such recovery furnaces include particulate matter, very odorous reduced sulfur compounds, and oxides of sulfur. Bleaching has

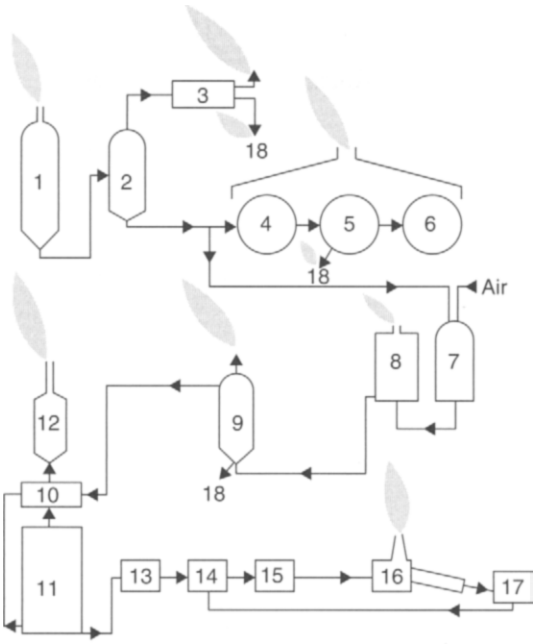


**Fig. 10.14.** Schematic diagram of the kraft pulping process [6]. 1, digester; 2, blow tank; 3, blow heat recovery; 4, washers; 5, screens; 6, dryers; 7, oxidation tower; 8, foam tank; 9, multiple effect evaporator; 10, direct evaporator; 11, recovery furnace; 12, electrostatic precipitator; 13, dissolver; 14, causticizer; 15, mud filter; 16, lime kiln; 17, slaker; 18, sewer.

been a substantial source of dioxins, but many processors have now modified their operations to use substantially less chlorine, greatly reducing the dioxin formation. If extensive and expensive control is not exercised over the kraft pulp process, the odors and aerosol emissions will affect a wide area. Odor complaints have been reported over 100 km away from these plants. A properly controlled and operated kraft plant will handle huge amounts of material and produce millions of kilograms of finished products per day, with little or no complaint regarding odor or particulate emissions.

## L. Noxious Trades

As the name implies, these operations, if uncontrolled, can cause a serious air pollution problem. The main problem is the odors associated with the process. Examples of such industries are tanning works, confined animal feeding operations (CAFOs), rendering plants, and many of the food processing plants such as fish meal plants. In most cases, the emissions of particulates and gases from such plants are not of concern, only the odors. However, other air pollutants are also common (e.g. chromium in tanning and nitric oxide (NO) near CAFOs). Requiring these industries to locate away from the business or residential areas is no longer acceptable as a means of control.

TABLE 10.5

**Emissions from Mobile Sources**

| Power plant type | Fuel | Major emissions | Vehicle type |
|---|---|---|---|
| Otto cycle | Gasoline | HC, CO, $CO_2$, $NO_x$ | Auto, truck, bus, aircraft, marine, motorcycle, tractor |
| Two-stroke cycle | Gasoline | HC, CO, $CO_2$, $NO_x$, particulate | Motorcycle, outboard motor |
| Diesel | Diesel oil | $NO_x$, particulate, $SO_x$, $CO_2$ | Auto, truck, bus, railroad, marine, tractor |
| Gas turbine (jet) | Turbine | $NO_x$, particulate, $CO_2$ | Aircraft, marine, railroad |
| Steam | Oil, coal | $NO_x$, $SO_x$, particulate, $CO_2$ | Marine |

## IV. MOBILE SOURCES

A mobile source of air pollution can be defined as one capable of moving from one place to another under its own power. According to this definition, an automobile is a mobile source and a portable asphalt batching plant is not. The regulatory definition seems to center around the internal combustion engine. Generally, mobile sources imply transportation, but sources such as construction equipment, gasoline-powered lawn mowers, and gasoline-powered tools are included in this category.

Mobile sources therefore consist of many different types of vehicles, powered by engines using different cycles, fueled by a variety of products, and emitting varying amounts of both simple and complex pollutants. Table 10.5 includes the more common mobile sources.

The predominant mobile air pollution source in all industrialized countries of the world is the automobile, powered by a four-stroke cycle (Otto cycle) engine and using gasoline as the fuel. In the United States, over 85 million automobiles were in use in 1990. If the 15 million gasoline-powered trucks and buses and the 4 million motorcycles are included, the United States total exceeds 100 million vehicles. The engine used to power these millions of vehicles has been said to be the most highly engineered machine of the century. When one considers the present reliability, cost, and life expectancy of the internal combustion engine, it is not difficult to see why it has remained so popular. A modern automotive engine traveling 100 000 km will have about $2.5 \times 10^8$ power cycles.

The emissions from a gasoline-powered vehicle come from many sources. Figure 10.15 illustrates what might be expected from an uncontrolled (1960 model) automobile and a controlled (1983 or later model) automobile if it complies with the 1983 federal standards [7]. With most of today's automobiles using unleaded gasoline, lead emissions are no longer a major concern in the West, but are still a problem in numerous other parts of the world.

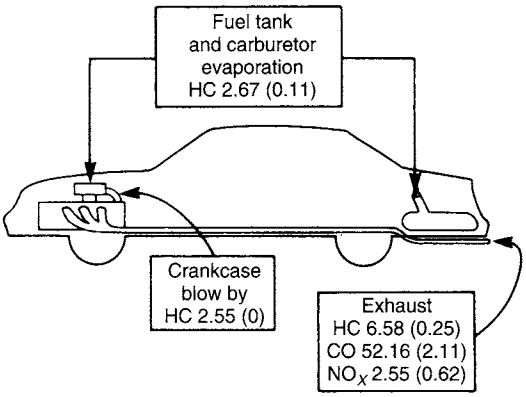


**Fig. 10.15.** Emissions from uncontrolled automobiles (and those meeting US EPA standards) in $g\,km^{-1}$.

## V. AIR TOXICS SOURCES

Hazardous air pollutants are known in most air pollution control communities as toxic air pollutants or air toxics. These are the pollutants that cause or are strongly suspected to cause cancer or other serious health effects, including reproductive and developmental effects or birth defects. They are also often associated with adverse environmental and ecological effects. The Clean Air Act Amendments of 1990 require the US Environmental Protection Agency (EPA) to control 188 air toxics (see Table 10.6). Examples of toxic air pollutants include benzene, which is found in gasoline; perchloroethlyene, which is emitted from some dry cleaning facilities; and methylene chloride, which is used as a solvent and paint stripper by a number of industries.

The Clean Air Act allows for petitions to modify the list (e.g. in 2006, caprolactam, hydrogen sulfide, and methyl ethyl ketone were undergoing modification).

Most air toxics originate from human-made sources, including mobile and stationary sources, similar to the criteria pollutants discussed in this chapter. However, many are predominantly or nearly exclusively indoor air pollutants.

Two types of stationary sources routinely emit air toxics:

1. *Major sources* emit 10 tons per year of any of the listed toxic air pollutants, or 25 tons per year of a mixture of air toxics. Major sources may release air toxics from equipment leaks, when materials are transferred from one location to another, or during discharge through emission stacks or vents.
2. *Area sources* are smaller-size facilities that release lesser quantities of air toxics. These sources emit less than 10 tons per year of a single air toxic, or less than 25 tons per year of a combination of air toxics. Though emissions from individual area sources are often relatively small, collectively their emissions can be of concern—especially in heavily populated communities with many sources.

**TABLE 10.6**

**Air Toxics Regulated by the US EPA**

| CAS number | Toxic air pollutant | Notes |
|---|---|---|
| 75070 | Acetaldehyde | |
| 60355 | Acetamide | |
| 75058 | Acetonitrile | |
| 98862 | Acetophenone | |
| 53963 | 2-Acetylaminofluorene | |
| 107028 | Acrolein | |
| 79061 | Acrylamide | |
| 79107 | Acrylic acid | |
| 107131 | Acrylonitrile | |
| 107051 | Allyl chloride | |
| 92671 | 4-Aminobiphenyl | |
| 62533 | Aniline | |
| 90040 | *o*-Anisidine | |
| 1332214 | Asbestos | |
| 71432 | Benzene (including benzene from gasoline) | |
| 92875 | Benzidine | |
| 98077 | Benzotrichloride | |
| 100447 | Benzyl chloride | |
| 92524 | Biphenyl | |
| 117817 | Bis(2-ethylhexyl)phthalate (DEHP) | |
| 542881 | Bis(chloromethyl)ether | |
| 75252 | Bromoform | |
| 106990 | 1,3-Butadiene | |
| 156627 | Calcium cyanamide | |
| 105602 | Caprolactam | Visit EPA website for current status of modification: http://www.epa.gov/ttn/atw/pollutants/atwsmod.html |
| 133062 | Captan | |
| 63252 | Carbaryl | |
| 75150 | Carbon disulfide | |
| 56235 | Carbon tetrachloride | |
| 463581 | Carbonyl sulfide | |
| 120809 | Catechol | |
| 133904 | Chloramben | |
| 57749 | Chlordane | |
| 7782505 | Chlorine | |
| 79118 | Chloroacetic acid | |
| 532274 | 2-Chloroacetophenone | |
| 108907 | Chlorobenzene | |
| 510156 | Chlorobenzilate | |
| 67663 | Chloroform | |
| 107302 | Chloromethyl methyl ether | |
| 126998 | Chloroprene | |
| 1319773 | Cresols/Cresylic acid (isomers and mixture) | |

(*continued*)

**TABLE 10.6** (*Continued*)

| CAS number | Toxic air pollutant | Notes |
|---|---|---|
| 95487 | *o*-Cresol | |
| 108394 | *m*-Cresol | |
| 106445 | *p*-Cresol | |
| 98828 | Cumene | |
| 94757 | 2,4-D, salts and esters | |
| 3547044 | DDE | |
| 334883 | Diazomethane | |
| 132649 | Dibenzofurans | |
| 96128 | 1,2-Dibromo-3-chloropropane | |
| 84742 | Dibutylphthalate | |
| 106467 | 1,4-Dichlorobenzene(*p*) | |
| 91941 | 3,3-Dichlorobenzidene | |
| 111444 | Dichloroethyl ether (bis(2-chloroethyl)ether) | |
| 542756 | 1,3-Dichloropropene | |
| 62737 | Dichlorvos | |
| 111422 | Diethanolamine | |
| 121697 | *N*,*N*-Diethyl aniline (*N*,*N*-dimethylaniline) | |
| 64675 | Diethyl sulfate | |
| 119904 | 3,3-Dimethoxybenzidine | |
| 60117 | Dimethyl aminoazobenzene | |
| 119937 | 3,3′-Dimethyl benzidine | |
| 79447 | Dimethyl carbamoyl chloride | |
| 68122 | Dimethyl formamide | |
| 57147 | 1,1-Dimethyl hydrazine | |
| 131113 | Dimethyl phthalate | |
| 77781 | Dimethyl sulfate | |
| 534521 | 4,6-Dinitro-*o*-cresol, and salts | |
| 51285 | 2,4-Dinitrophenol | |
| 121142 | 2,4-Dinitrotoluene | |
| 123911 | 1,4-Dioxane (1,4-diethyleneoxide) | |
| 122667 | 1,2-Diphenylhydrazine | |
| 106898 | Epichlorohydrin (l-chloro-2,3-epoxypropane) | |
| 106887 | 1,2-Epoxybutane | |
| 140885 | Ethyl acrylate | |
| 100414 | Ethyl benzene | |
| 51796 | Ethyl carbamate (urethane) | |
| 75003 | Ethyl chloride (chloroethane) | |
| 106934 | Ethylene dibromide (dibromoethane) | |
| 107062 | Ethylene dichloride (1,2-dichloroethane) | |
| 107211 | Ethylene glycol | |
| 151564 | Ethylene imine (aziridine) | |
| 75218 | Ethylene oxide | |
| 96457 | Ethylene thiourea | |
| 75343 | Ethylidene dichloride (1,1-dichloroethane) | |

(*continued*)

**TABLE 10.6** (*Continued*)

| CAS number | Toxic air pollutant | Notes |
|---|---|---|
| 50000 | Formaldehyde | |
| 76448 | Heptachlor | |
| 118741 | Hexachlorobenzene | |
| 87683 | Hexachlorobutadiene | |
| 77474 | Hexachlorocyclopentadiene | |
| 67721 | Hexachloroethane | |
| 822060 | Hexamethylene-1,6-diisocyanate | |
| 680319 | Hexamethylphosphoramide | |
| 110543 | Hexane | |
| 302012 | Hydrazine | |
| 7647010 | Hydrochloric acid | |
| 7664393 | Hydrogen fluoride (hydrofluoric acid) | |
| 7783064 | Hydrogen sulfide | Visit EPA website for current status of modification: http://www.epa.gov/ttn/atw/pollutants/atwsmod.html |
| 123319 | Hydroquinone | |
| 78591 | Isophorone | |
| 58899 | Lindane (all isomers) | |
| 108316 | Maleic anhydride | |
| 67561 | Methanol | |
| 72435 | Methoxychlor | |
| 74839 | Methyl bromide (bromomethane) | |
| 74873 | Methyl chloride (chloromethane) | |
| 71556 | Methyl chloroform (1,1,1-trichloroethane) | |
| 78933 | Methyl ethyl ketone (2-butanone) | Visit EPA website for current status of modification: http://www.epa.gov/ttn/atw/pollutants/atwsmod.html |
| 60344 | Methyl hydrazine | |
| 74884 | Methyl iodide (iodomethane) | |
| 108101 | Methyl isobutyl ketone (hexone) | |
| 624839 | Methyl isocyanate | |
| 80626 | Methyl methacrylate | |
| 1634044 | Methyl tert butyl ether | |
| 101144 | 4,4-Methylene bis(2-chloroaniline) | |
| 75092 | Methylene chloride (dichloromethane) | |
| 101688 | Methylene diphenyl diisocyanate (MDI) | |
| 101779 | 4,4-Methylenedianiline | |
| 91203 | Naphthalene | |
| 98953 | Nitrobenzene | |
| 92933 | 4-Nitrobiphenyl | |
| 100027 | 4-Nitrophenol | |
| 79469 | 2-Nitropropane | |
| 684935 | *N*-Nitroso-*N*-methylurea | |

(*continued*)

**TABLE 10.6** (*Continued*)

| CAS number | Toxic air pollutant | Notes |
|---|---|---|
| 62759 | *N*-Nitrosodimethylamine | |
| 59892 | *N*-Nitrosomorpholine | |
| 56382 | Parathion | |
| 82688 | Pentachloronitrobenzene (quintobenzene) | |
| 87865 | Pentachlorophenol | |
| 108952 | Phenol | |
| 106503 | *p*-Phenylenediamine | |
| 75445 | Phosgene | |
| 7803512 | Phosphine | |
| 7723140 | Phosphorus | |
| 85449 | Phthalic anhydride | |
| 1336363 | Polychlorinated biphenyls (aroclors) | |
| 1120714 | 1,3-Propane sultone | |
| 57578 | beta-Propiolactone | |
| 123386 | Propionaldehyde | |
| 114261 | Propoxur (baygon) | |
| 78875 | Propylene dichloride (1,2-dichloropropane) | |
| 75569 | Propylene oxide | |
| 75558 | 1,2-Propylenimine (2-methyl aziridine) | |
| 91225 | Quinoline | |
| 106514 | Quinone | |
| 100425 | Styrene | |
| 96093 | Styrene oxide | |
| 1746016 | 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin | |
| 79345 | 1,1,2,2-Tetrachloroethane | |
| 127184 | Tetrachloroethylene (perchloroethylene) | |
| 7550450 | Titanium tetrachloride | |
| 108883 | Toluene | |
| 95807 | 2,4-Toluene diamine | |
| 584849 | 2,4-Toluene diisocyanate | |
| 95534 | *o*-Toluidine | |
| 8001352 | Toxaphene (chlorinated camphene) | |
| 120821 | 1,2,4-Trichlorobenzene | |
| 79005 | 1,1,2-Trichloroethane | |
| 79016 | Trichloroethylene | |
| 95954 | 2,4,5-Trichlorophenol | |
| 88062 | 2,4,6-Trichlorophenol | |
| 121448 | Triethylamine | |
| 1582098 | Trifluralin | |
| 540841 | 2,2,4-Trimethylpentane | |
| 108054 | Vinyl acetate | |
| 593602 | Vinyl bromide | |
| 75014 | Vinyl chloride | |

(*continued*)

**TABLE 10.6** (*Continued*)

| CAS number | Toxic air pollutant | Notes |
|---|---|---|
| 75354 | Vinylidene chloride (1,1-dichloroethylene) | |
| 1330207 | Xylenes (isomers and mixture) | |
| 95476 | *o*-Xylenes | |
| 108383 | *m*-Xylenes | |
| 106423 | *p*-Xylenes | |
| 0 | Antimony compounds | |
| 0 | Arsenic compounds (inorganic including arsine) | |
| 0 | Beryllium compounds | |
| 0 | Cadmium compounds | |
| 0 | Chromium compounds | |
| 0 | Cobalt compounds | |
| 0 | Coke oven emissions | |
| 0 | Cyanide compounds | X'CN where X = H' or any other group where a formal dissociation may occur. For example KCN or $Ca(CN)_2$ |
| 0 | Glycol ethers | Includes mono- and di-ethers of ethylene glycol, diethylene glycol, and triethylene glycol R-$(OCH_2CH_2)n$-OR' where |
| 0 | Lead compounds | |
| 0 | Manganese compounds | |
| 0 | Mercury compounds | |
| 0 | Fine mineral fibers | Includes mineral fiber emissions from facilities manufacturing or processing glass, rock, or slag fibers (or other mineral derived fibers) of average diameter 1 μm or less |
| 0 | Nickel compounds | |
| 0 | Polycyclic organic matter | Includes organic compounds with more than one benzene ring, and which have a boiling point greater than or equal to 100°C |
| 0 | Radionuclides (including radon) | A type of atom which spontaneously undergoes radioactive decay |
| 0 | Selenium compounds | |

*Notes*: For all listings above which contain the word "compounds" and for glycol ethers, the following applies: unless otherwise specified, these listings are defined as including any unique chemical substance that contains the named chemical (i.e., antimony, arsenic, etc.) as part of that chemical's infrastructure. $n$ = 1, 2, or 3; R = alkyl or aryl groups; and R' = R, H, or groups which, when removed, yield glycol ethers with the structure: R-$(OCH_2CH)n$-OH. Polymers are excluded from the glycol category.

The 1990 Clean Air Act Amendments direct the EPA to set standards for all major sources of air toxics (and some area sources that are of particular concern). The EPA published the initial list of source categories in 1992 in the *Federal Register* (57FR31576, July 16, 1992), which has since been revised and

updated frequently. The list designates whether the sources are considered to be major or area sources.

## VI. EMISSION INVENTORY

An *emission inventory* is a list of the amount of pollutants from all sources entering the air in a given time period. The boundaries of the area are fixed [8].

The tables of emission inventory are very useful to control agencies as well as planning and zoning agencies. They can point out the major sources whose control can lead to a considerable reduction of pollution in the area. They can be used with appropriate mathematical models to determine the degree of overall control necessary to meet ambient air quality standards. They can be used to indicate the type of sampling network and the locations of individual sampling stations if the areas chosen are small enough. For example, if an area uses very small amounts of sulfur-bearing fuels, establishing an extensive $SO_2$ monitoring network in the area would not be an optimum use of public funds. Emission inventories can be used for publicity and political purposes: "If natural gas cannot meet the demands of our area, we will have to burn more high-sulfur fuel, and the $SO_2$ emissions will increase by 8 tons per year."

The method used to develop the emission inventory does have some elements of error, but the other two alternatives are expensive and subject to their own errors. The first alternative would be to monitor continually every major source in the area. The second method would be to monitor continually the pollutants in the ambient air at many points and apply appropriate diffusion equations to calculate the emissions. In practice, the most informative system would be a combination of all three, knowledgeably applied.

The US Clean Air Act Amendments of 1990 [9] strengthened the emission inventory requirements for plans and permits in nonattainment areas. The amendments state:

> INVENTORY—Such plan provisions shall include a comprehensive, accurate, current inventory of actual emissions from all sources of the relevant pollutant or pollutants in such area, including such periodic revisions as the Administrator may determine necessary to assure that the requirements of this part are met.
>
> IDENTIFICATION AND QUANTIFICATION—Such plan provisions shall expressly identify and quantify the emissions, if any, of any such pollutant or pollutants which will be allowed, from the construction and operation of major new or modified stationary sources in each such area. The plan shall demonstrate to the satisfaction of the Administrator that the emissions quantified for this purpose will be consistent with the achievement of reasonable further progress and will not interfere with the attainment of the applicable national ambient air quality standard by the applicable attainment date.

### A. Inventory Techniques

To develop an emission inventory for an area, one must (1) list the types of sources for the area, such as cupolas, automobiles, and home fireplaces;

(2) determine the type of air pollutant emission from each of the listed sources, such as particulates and $SO_2$; (3) examine the literature [10] to find valid emission factors for each of the pollutants of concern (e.g. "particulate emissions for open burning of tree limbs and brush are 10 kg per ton of residue consumed"); (4) through an actual count, or by means of some estimating technique, determine the number and size of specific sources in the area (the number of steelmaking furnaces can be counted, but the number of home fireplaces will probably have to be estimated); and (5) multiply the appropriate numbers from (3) and (4) to obtain the total emissions and then sum the similar emissions to obtain the total for the area.

A typical example will illustrate the procedure. Suppose we wish to determine the amount of carbon monoxide from oil furnaces emitted per day, during the heating season, in a small city of 50 000 population:

1. The source is oil furnaces within the boundary area of the city.
2. The pollutant of concern is carbon monoxide.
3. Emission factors for carbon monoxide are listed in various ways [10] (240 g per 1000 L of fuel oil, 50 g per day per burner, 1.5% by volume of exhaust gas, etc.). For this example, use 240 g per 1000 L of fuel oil.
4. Fuel oil sales figures, obtained from the local dealers association, average 40 000 L per day.
5. $$\frac{240\,\text{g CO}}{1000\,\text{L}} \times \frac{40\,000\,\text{L}}{\text{day}} = 9.6\,\text{kg CO/day}$$

## B. Emission Factors

Valid emission factors for each source of pollution are the key to the emission inventory. It is not uncommon to find emission factors differing by 50%, depending on the researcher, variables at the time of emission measurement, etc. Since it is possible to reduce the estimating errors in the inventory to $\pm 10\%$ by proper statistical sampling techniques, an emission factor error of 50% can be overwhelming. It must also be realized that an uncontrolled source will emit at least 10 times the amount of pollutants released from one operating properly with air pollution control equipment installed.

Actual emission data are available from many handbooks, government publications, and literature searches of appropriate research papers and journals. In addition, online support is available, especially the Technology Transfer Network/Clearinghouse for Inventories and Emissions Factors, accessible at http://www.epa.gov/ttn/chief/index.html. This site provides information on emission factors, inventory, modeling, along with a knowledge base for emissions monitoring.

It is always wise to verify the data, if possible, as to the validity of the source and the reasonableness of the final number. Some emission factors, which have been in use for years, were only rough estimates proposed by someone years ago to establish the order of magnitude of the particular source.

Emission factors must be also critically examined to determine the tests from which they were obtained. For example, carbon monoxide from an automobile will vary with the load, engine speed, displacement, ambient temperature, coolant temperature, ignition timing, carburetor adjustment, engine condition, etc. However, in order to evaluate the overall emission of carbon monoxide to an area, we must settle on an average value that we can multiply by the number of cars, or kilometers driven per year, to determine the total carbon monoxide released to the area.

### C. Data Gathering

To compile the emission inventory requires a determination of the number and types of units of interest in the study area. It would be of interest, for example, to know the number of automobiles in the area and the number of kilometers each was driven per year. This figure would require considerable time and expense to obtain. Instead, it can be closely approximated by determining the liters of gasoline sold in the area during the year. Since a tax is collected on all gasoline sold for highway use, these figures can be obtained from the tax collection office.

Data regarding emissions are available from many sources. Sometimes the same item may be checked by asking two or more agencies for the same information. An example of this would be to check the liters of gasoline sold in a county by asking both the tax office and the gasoline dealers association. Sources of information for an emission inventory include: (1) city, county, and state planning commissions; (2) city, county, and state chambers of commerce; (3) city, county, and state industrial development commissions; (4) census bureaus; (5) national associations such as coal associations; (6) local associations such as the County Coal Dealers Association; (7) individual dealers or distributors of oil, gasoline, coal, etc.; (8) local utility companies; (9) local fire and building departments; (10) data gathered by air pollution control agencies through surveys, sampling, etc.; (11) traffic maps; and (12) insurance maps.

### D. Data Reduction and Compilation

The final emission inventory can be prepared on a computer. This will enable the information to be stored on magnetic tape or disk so that it can be updated rapidly and economically as new data or new sources appear. The computer program can be written so that changes can easily be made. There will be times when major changes occur and the inventory must be completely changed. Imagine the change that would take place when natural gas first becomes available in a commercial–residential area which previously used oil and coal for heating.

To determine emission data, as well as the effect that fuel changes would produce, it is necessary to use the appropriate thermal conversion factor from one fuel to another. Table 10.7 lists these factors for fuels in common use.

TABLE 10.7

**Thermal Conversion Factors for Fuels**

| Fuel | Joule $\times 10^6$ |
|---|---|
| Bituminous coal | 30.48 per kg |
| Anthracite coal | 29.55 per kg |
| Wood | 20.62 per kg |
| Distillate fuel oil | 38.46 per kg |
| Residual fuel oil | 41.78 per L |
| Natural gas | 39.08 per $m^3$ |
| Manufactured gas | 20.47 per $m^3$ |

A major change in the emissions for an area will occur if control equipment is installed. This can be shown in the emission inventory to illustrate the effect on the community.

By keeping the emission inventory current and updating it at least yearly as fuel uses change, industrial and population changes occur, and control equipment is added, a realistic record for the area is obtained.

## VII. AN INTERNATIONAL PERSPECTIVE: DIFFERENCES IN TIME AND SPACE

Western Civilization is often criticized for its disproportionate demand for fuel, especially nonrenewable fossil fuels. The way that a nation addresses energy use is an important measure of how advanced it is, not only in dealing with pollution, but the level of sophistication of its economic systems. As evidence, many poorer nations are confronted with the choice of saving sensitive habitat or allowing large-scale biomass burns. And, the combustion processes in developing countries are usually much less restrictive than those in more developed nations.

This chapter addresses some of the major sources of air pollution from the perspective of the highly industrialized nations. However, industrial processes can vary significantly between developed and underdeveloped nations. For example, in Canada and the United States, the major sources of dioxins, a chemical group comprising some of the world's most toxic and carcinogenic compounds, range from dispersed activities, such as trash burning, to heavy industry (see Fig. 10.16). The major sources of dioxin emissions in Latin America are distributed quite differently than those in Canada and US. Actual emission inventories are being developed, but preliminary information indicates that much of the dioxin produced in Mexico, for example, is from backyard burning, such as neighborhood scale brick making. Refractory in developing nations are often small-scale, neighborhood operations. Often, the heat sources used to reach refractory temperatures are furnaces with

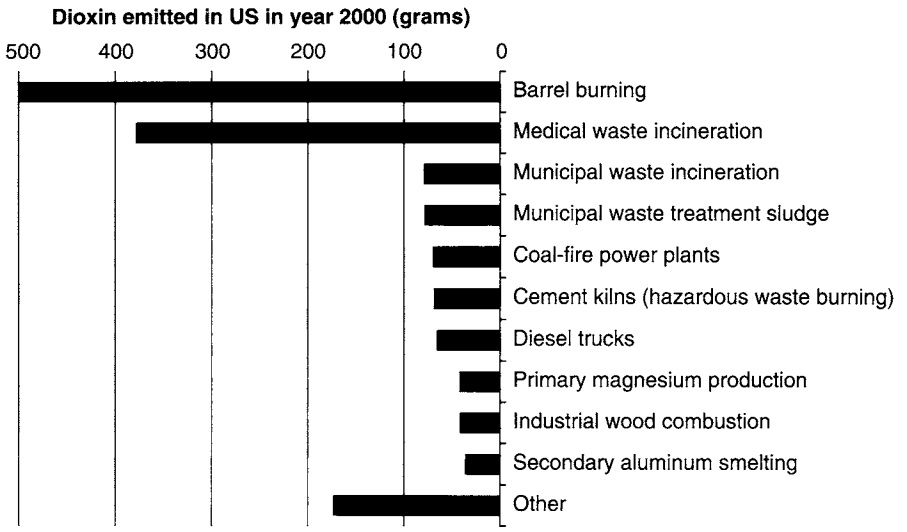


**Fig. 10.16.** Industrial categories of dioxin emitters in the United States in 2000. *Source*: US Environmental Protection Agency, 2005, The Inventory of Sources of Dioxin in the United States (External Review Draft); accessed on June 12, 2006 at: http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=132080.

scrapped materials as fuel, especially petroleum-derived substances like automobile tires. This not only is important to the country in which the combustion occurs, but can be an international concern when the burning is near borders. This is the case for the metropolitan area of El Paso, Texas, and Ciudad Juarez, Mexico, with a combined population of two million. The cities are located in a deep canyon between two mountain ranges, which can contribute to thermal inversions in the atmosphere (see Fig. 10.17). The air quality has been characterized by the US EPA as seriously polluted, with brick making on the Mexican side identified as a major source.[4]

In Mexico, workers who make bricks are called *ladrilleros*. Many *ladrilleros* live in unregulated settlements known as *colonias* on the outskirts of Ciudad Juarez. The kilns, using the same design as those in Egypt thousands of years ago, are located within these neighborhoods, next to the small houses. The *ladrilleros* are not particular about the fuel, burning anything with caloric value, including scrap wood and old tires, as well as more conventional fuels like methane and butane. The dirtier fuels, like the tires, release large black plumes of smoke that contains a myriad of contaminants.

Children are at elevated risk of health problems when exposed to these plumes, since their lungs and other organs are undergoing prolific tissue growth. Thus, the *ladrilleros'* families have particularly elevated risks due to

[4] The major source of information about Rio Grande brick making is *Environmental Health Perspectives*, Vol. 104, Number 5, May 1996.

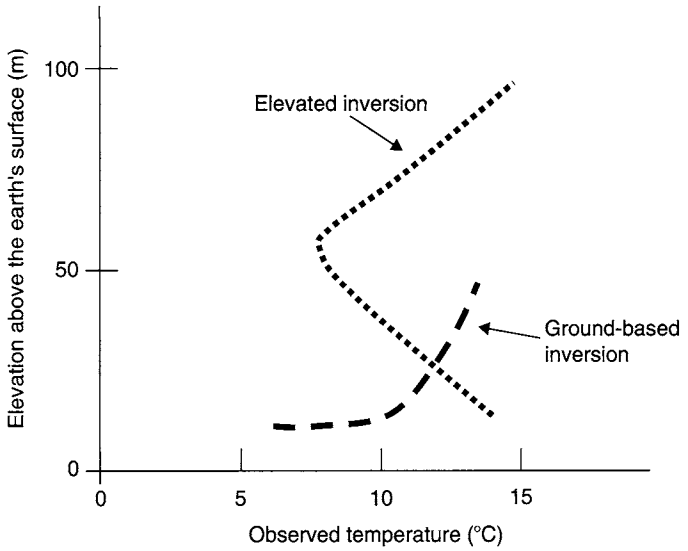


**Fig. 10.17.** Two types of thermal inversions that contribute to air pollution.

their frequent and high dose exposures. "The health impact is not only of concern to the worker but also the entire family, especially pregnant women and children who, because of their socioeconomic status, tend to be undernourished," according to Beatriz Vera, project coordinator for the US–Mexico Border Environment and Health Projects. She adds that "many times the entire family participates in the process. Sometimes children are put directly into the area where the kiln is fired."

The two nations' governments appear to recognize the problem, as do numerous nongovernmental organizations (NGOs). These have included Environmental Defense (ED), Physicians for Social Responsibility, the Federacion Mexicana de Asociaciones Privadas de Salud y Desarrollo Comunitario (FEMAP), and El Paso Natural Gas (EPNG). For example, FEMAP and EPNG offer courses to the *ladrilleros* from throughout the region on ways to use higher quality fuel, including improved safety and business practices as well. Often, however, even if the brick makers know about cleaner fuels, they cannot afford them. For example, they have used butane, but in 1994 the Mexican government started to phase out its subsidy and about the same time the peso was devalued, leading to a sharp increase in butane costs. The *ladrilleros* were forced to return to using the cheaper fuels. In the meantime the Mexican government banned the burning of tires, so much of the more recent tire burning has been done surreptitiously at night.

A number of solutions to the problem have been proposed, including more efficient kilns. However, arguably the best approach is to prevent the combustion in the first place. In fact, many of the traditional villages where bricks are now used were previously constructed with adobe. A return to such a noncombustion approach could hold the key. The lesson here is that

often in developing countries the simpler, "low-tech" solutions are the most sustainable.

In the mid-1990s, the US EPA and the Texas Natural Resource Conservation Commission (TNRCC) conducted a study in the Rio Grande valley region to address concerns about the potential health impact of local air pollutants, and especially since little air quality information was available at the time. There are numerous "cottage industries," known as *maquiladoras*,[5] along both sides of the Texas–Mexico border as ascribed by the Rio Grande. In particular, the study addressed the potential for air pollution to move across the US–Mexican border into the southern part of Texas. Air pollution and weather data were collected for a year at three fixed sites near the border in and near Brownsville, Texas. The study found overall levels of air pollution to be similar to or even lower than other urban and rural areas in Texas and elsewhere and that transport of air pollution across the border did not appear to adversely impact air quality across the US border.

Many developing countries are evolving into industrialized nations. Not long ago in the US, the standard means of getting rid of household trash was the daily burn. Each evening, people in rural areas, small towns, and even larger cities, made a trip to the backyard, dumped the trash they had accumulated into a barrel,[6] and burned the contents. Also, burning was a standard practice elsewhere, such as intentional fires to remove brush, and the previously mentioned "cottage industries" like backyard smelters and metal recycling operations. Beginning in the 1960s and 1970s, the public acceptance

[5] The Coalition for Justice in the Maquiladoras, a cross-border group that organizes maquiladora workers, traces the term maquiladora to *maquilar*, a popular form of the verb maquinar that roughly means "to submit something to the action of a machine," as when rural Mexicans speak of maquilar with regard to the grain that is transported to a mill for processing. The farmer owns the grain; yet someone else owns the mill who keeps a portion of the value of the grain for milling. So, the origin of maquiladora can be found in this division of labor. The term has more recently been applied to the small factories opened by US companies to conduct labor-intensive jobs on the Mexican side of the border. Thus, maquilar has changed to include this process of labor, especially assembling parts from various sources, and the maquiladoras are those small assembling operations along the border.

While the maquiladoras have provided opportunities to entrepreneurs along the Mexico–US border, they have also given opportunity for the workers and their families to be exploited in the interests of profit and economic gain.

[6] Often, these barrels were the 55-gallon drum variety, so the first burning likely volatilized some very toxic compounds, depending on the residues remaining in the drum. These contents could have been solvents (including halogenated compounds like chlorinated aliphatics and aromatics), plastic residues (like phthalates), and petroleum distillates. They may even have contained substances with elevated concentrations of heavy metals, like mercury, lead, cadmium, and chromium. The barrels (drums) themselves were often perforated to allow for higher rates of oxidation (combustion) and to take advantage of the smokestack effect (i.e. driving the flame upward and pushing the products of incomplete combustion out of the barrel and into the plume). I recall that in the 1960s my neighbors not being happy about people in the neighborhood burning trash while their wash was drying on the clothesline. They would complain of ash (aerosols) blackening their clothes and the odor from the incomplete combustion products on their newly washed laundry. Both of these complaints are evidence that the plume leaving the barrel contained harmful contaminants.

and tolerance for open burning was waning. Local governments began to restrict and eventually to ban many fires. Often, these restrictions had multiple rationales, especially public safety (fires becoming out of control, especially during dry seasons) and public health (increasing awareness of the association between particulate matter in the air and diseases like asthma and even lung cancer).

Emissions depend on the source material being burned. For example, when halogenated organic compounds are burned, some highly toxic compounds are released. To illustrate, let us consider the processing of polyvinyl chloride (PVC). PVC is a polymer, like polyethylene. However, rather than a series of ethylenes in the backbone chain, a chlorine atom replaces the hydrogen on each of the ethylene groups by free radical polymerization of vinyl chloride. The first thing that can happen when PVC is heated is that the polymers become unhinged and chlorine is released (see Fig. 10.18). Also, the highly toxic and carcinogenic dioxins and furans can be generated from the thermal breakdown and molecular rearrangement of PVC in a heterogeneous process, i.e. the reaction occurs in more than one phase (in this case, in the solid and gas phases). The active sorption sites on the particles allow for the chemical reactions, which are catalyzed by the presence of inorganic chloride compounds and ions sorbed to the particle surface. The process occurs within the temperature range, 250–450°C, so most of the dioxin formation under the precursor mechanism occurs away from the high temperature of the fire, where the gases and smoke derived from combustion of the organic materials have cooled. Dioxins and furans may also form *de novo*, wherein dioxins are formed from moieties different from those of the molecular structure of dioxins, furans, or precursor compounds. The process needs a chlorine donor (a molecule that "donates" a chlorine atom to the precursor molecule). This leads to the formation and chlorination of a chemical intermediate that is a precursor.

In addition, PVC is seldom in a pure form. In fact, most wires have to be pliable and flexible. On its own, PVC is rigid, so plasticizers must be added, especially phthalates. These compounds have been associated with chronic effects in humans including endocrine disruption. Also, since PVC catalyzes its own decomposition, metal stabilizers have been added to PVC products. These have included lead, cadmium, and tin (e.g. butylated forms). Another very common class of toxic compounds released when plastics are burned are the PAHs.

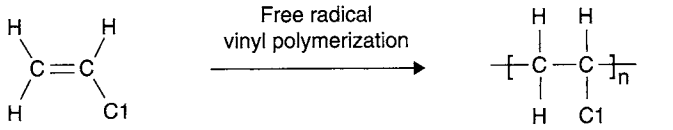


**Fig. 10.18.** Free radical polymerization of vinyl chloride to form PVC.

Like open burning, emissions from industrial stacks can be pervasive and contained myriad toxic components. People living in the plume of industries like coke ovens experience the obnoxious smelling compounds, including metallic and sulfur compounds that volatilized during the conversion of coal to coke needed for steel manufacturing. While such areas continue to be industrialized, such ambient air quality as that in the 1960s is no longer tolerated in the West.

Other sources in developing countries are distributed, such as burning tire piles and junkyards. Again, this can be similar to conditions in the West a half century ago. And, they continue in some lower socioeconomic communities to this day. In fact, the combination of fires, wet muck (composed of soil, battery acid, radiator fluids, motor oil, corroded metal, and water), and oxidizing metals created a rather unique odor around the yards.

## VIII. ODORS: MORE THAN JUST A NUISANCE

A number of the processes discussed in this chapter produce odors. Odors have often been associated with public health nuisances. In addition to the link between memory and olfactory centers, however, the nasal–neural connection is important to environmental exposure. This goes beyond nuisance and is an indication of potential adverse health effects. For example, nitric oxide (NO) is a neurotoxic gas released from many sources, such as confined animal feeding operations, breakdown of fertilizers after they are applied to the soil and crops, and emissions from vehicles. Besides being inhaled into the lungs, NO can reach the brain directly. The gas can pass through a thin membrane via the nose to the brain.

The nasal exposure is a different paradigm from that usually used to calculate exposure. In fact, most sources do not have a means for calculating exposures other than dermal, inhalation, and ingestion. People who live near swine and poultry facilities can be negatively affected when they smell odors from the facility. This is consistent with other research that has found that people experience adverse health symptoms more frequently when exposed to livestock odors. These symptoms include eye, nose, and throat irritation, headache, nausea, diarrhea, hoarseness, sore throat, cough, chest tightness, nasal congestion, palpitations, shortness of breath, stress, and drowsiness. There is quite a bit of diversity in response, with some people being highly sensitive to even low concentrations of odorant compounds while others are relatively unfazed even at much higher concentrations.

Actually, response to odors can be triggered by three different mechanisms. In the first mechanism, symptoms can be induced by exposure to odorant compounds at sufficiently high concentrations to cause irritation or other toxicological effects. The irritation, not the odor, evokes the health symptoms. The odor sensation is merely as an exposure indicator. In the second mechanism, symptoms of adverse effects result from odorants concentrations lower than

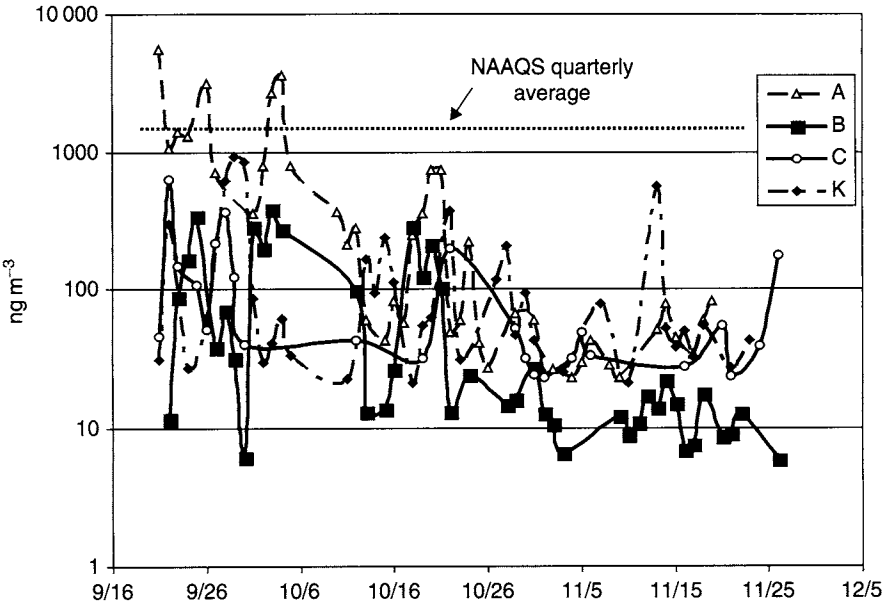


**Fig. 10.19.** Lead concentrations (composition of $PM_{2.5}$) at the World Trade Center site in 2001. NAAQS: The National Ambient Air Quality Standard for lead, i.e. $1.55\,\mu g\,m^{-3}$ averaged each quarter.

those eliciting irritation. This can be owing to genetic predisposition or conditioned aversion. In the third mechanism, symptoms can result from a coexisting pollutant, e.g. an endotoxin, which is a component of the odorant mixture.

Therefore, to address this new paradigm, better technologies will be needed. For example, innovative research is helping to make odor measurements more quantifiable, such as the development of "artificial noses."[7]

During the aftermath of the World Trade Center attacks, odors played a key role in response. People were reminded daily of the traumatic episode, even when the smoke from the fire was not visible. And, the odors were evidence of exposure to potentially toxic substances. In this instance, it was not NO, but volatile, semivolatile organic, and metallic compounds. The presence of the odors was one of many factors that kept New Yorkers on edge and until they significantly subsided, they continued to be a source of anxiety. Analysis of the samples confirmed my brain's olfactory–memory connection. The plume from the World Trade Center fires contained elevated concentrations of PAHs, dioxins, furans, VOCs (e.g. benzene), and particles containing metals (see Fig. 10.19). The elevated levels of these air pollutants persisted well after the attacks on September 11, 2001.

[7] For a survey of the state-of-the-science in electronic odor sensing technologies, see Nagle, H. T., Schiffman, S. S., and Gutierrez-Osuna, R., The how and why of electronic notes. *IEEE Spectr.* 35(9), 22–34 (1998).

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## QUESTIONS

1. Calculate the heat generated by dissociation and formation as one molecular weight of methane, $CH_4$, burns to carbon dioxide and water. How does this heating value compare to the tabular heating value for methane?
2. Many control districts have banned the use of private backyard incinerators. Would you expect a noticeable increase in air quality as a result of this action?
3. Show a free radical reaction which results in ethane in the effluent of a combustion process burning pure methane with pure oxygen.
4. A power plant burns oil that is 4% ash and 3% sulfur. At 50% excess air, what particulate ($mg\,m^{-3}$) would you expect?
5. Many control districts have very tight controls over petroleum refineries. Suppose these refineries produce 100 million liters of products per day and required air pollution control devices to recover all of the 2% which was previously lost. What are the savings in dollars per year at an average product cost of 10 cents per liter? How does this compare to the estimate that the refineries spent $400 million for control equipment over a 10-year period?
6. Suppose a 40 000-liter gasoline tank is filled with liquid gasoline with an average vapor pressure of 20 mm Hg. At 50% saturation, what weight of gasoline would escape to the atmosphere during filling?
7. If a major freeway with four lanes of traffic in one direction passes four cars per second at 100 km per hour during the rush period, and each car carries two people, how often would a commuter train of five cars carrying 100 passengers per car have to be operated to handle the same load? Assume the train would also operate at 100 km per hour.
8. An automobile traveling 50 km per hour emits 0.1% CO from the exhaust. If the exhaust rate is $80\,m^3$ per minute, what is the CO emission in grams per kilometer?
9. List the following in increasing amounts from the exhaust of an idling automobile: $O_2$, $NO_x$, $SO_x$, $N_2$, unburned hydrocarbons, $CO_2$, and CO.
10. What technologies can be adapted to moderate the increased air pollution associated with industrial development in developing nations? What are some of the important things to keep in mind when transferring such technologies to other cultures?
11. Identify two air pollutants wherein odor may be a promising indicator of air quality. What are the limitations of using odor beyond a screening level?
12. Consider the following information from an accident report filed with the US EPA and write a brief contingency plan that would prevent such an incident occurring at any refinery:

    At about 10:15 a.m., on October 16, 1995, an explosion and fire occurred at Plant No. 1 of the Pennzoil Products Company refinery in Rouseville, Pennsylvania. After the initial explosion, flames quickly engulfed a large area of the refinery, including areas under construction, storage trailers, a trailer where contractors took work breaks, and many storage tanks. The flames ignited several tanks containing naphtha and fuel oil. During the fire, several loud explosions could be heard as compressed gas cylinders and other sealed containers exploded.

    The explosions hurled some plant debris beyond the fenceline. Thick black smoke spread throughout the area. The fire forced Pennzoil employees and contractors at the plant, residents of the town of Rouseville and an elementary school, and the Pennzoil office across Route 8 from the facility, to evacuate. Firefighters extinguished the fire at about 12:30 p.m. that same day. Three workers were killed in the fire and three others were injured. Two of the injured died later as a result of their injuries. The fire resulted in extensive damage to the facility. Minor "sheening" was reported on the stream that runs past the refinery, but there were no reports of any materials spilled into the stream or environmental damage.

    A welding operation was in progress on a service stairway located between two waste liquid storage tanks (tanks 487 and 488) at the time of the incident. These tanks contained mixtures of waste hydrocarbons and water. A hot work (welding, cutting) permit had been

prepared, as required by Occupational Safety and Health Administration (OSHA) standard, which included combustible gas detection prior to welding to ensure the safety of the work.

The EPA Chemical Accident Investigation Team (CAIT) identified the immediate cause of the fire and the conditions which triggered the serious consequences. The immediate cause of the fire was the ignition of flammable vapors in storage tank 487. Although the CAIT could not determine the exact mechanism, there are at least two likely scenarios: undetected flammable vapors emitted from tank 487 were ignited by an ignition source which then flashed back into the tank; or an electrical discharge in the tank 487, generated by the arc welding, ignited flammable vapors in the tank.