

Chapter 8 Quantification of Exposure: Dispersion, Transport, and Fate of Air Toxics in the Atmosphere

Table of Contents

8.1	Introduction	1
8.2	Dispersion and Atmospheric Transport of Air Pollutants	1
8.2.1	General Types of Releases	2
8.2.2	Characteristics of Releases that Affect Dispersion and Transport	3
8.2.3	Physical and Meteorological Factors Affecting Air Toxics Dispersion and Transport ..	7
8.3	Fate of Air Toxics in the Atmosphere	13
8.3.1	Physical Processes Removing Air Toxics	13
8.3.2	Chemical Reactions that Remove Air Toxics	15
8.3.3	Chemical Reactions that Result in the Secondary Formation of Pollutants	16
8.3.4	Overall Persistence of Air Toxics in the Atmosphere	17
	References	19

8.1 Introduction

This chapter describes the major physical processes that affect the movement of air toxics through the atmosphere. Section 8.1 describes the mechanisms through which sources release air toxics into the air and how specific release characteristics and meteorological factors affect air toxics dispersion and transport. Section 8.2 discusses the major physical and chemical processes that affect the fate of air toxics, including deposition and chemical reaction. The discussion of air toxics fate in this chapter is focused on describing the presence of air toxics in the atmosphere and processes that influence this presence. The fate of deposited air toxics in other media and ecosystems is included in Chapter 17.

The atmosphere and atmospheric processes is a complex and expansive subject. An understanding of at least the rudiments of this subject is central to an understanding of how air toxics disperse and persist or are removed once released to the air. Appendix G provides an overview of atmospheric and meteorological concepts and terms relevant to this chapter. Appendix G also provides information on sources of meteorological data for modeling air toxics dispersion and transport. Whenever possible, it is recommended that a meteorologist be part of the risk assessment technical team.

8.2 Dispersion and Atmospheric Transport of Air Pollutants

Several characteristics of the source can affect the movement of air toxics while they are still close to the source (e.g., source height, gas exit temperature). Once air toxics are transported beyond the immediate vicinity of the source, atmospheric and meteorological factors (particularly wind speed and direction) govern air toxics dispersion and transport. This section describes how the movement of air toxics is affected by source characteristics, chemical properties, and atmospheric processes.

Dispersion, Transport, and Fate: What's the Difference?

Dispersion is a term applied to air toxics releases that means to spread or distribute from a source, with (generally) a decrease in concentration with distance from the source. Dispersion is affected by a number of factors including characteristics of the source, the pollutants, and ambient atmospheric conditions.

Transport is a term that refers to the processes (e.g., winds) that carry or cause pollutants to move from one location to another, especially over some distance.

Fate of air pollution refers to three things:

- Where a pollutant ultimately ends up (e.g., air distant from the source, soil, water, fish tissue);
- How long it persists in the environment; and
- The chemical reactions which it undergoes.

The fate of an air pollutant is governed both by transport processes and by the characteristics of the pollutant (e.g., its persistence, its ability to undergo reaction, and tendency to accumulate in water or soil, or to concentrate in the food chain).

8.2.1 General Types of Releases

The discussion of air toxics sources in Chapter 4 described air toxics emissions from a regulatory perspective (e.g., “stationary” versus “mobile” sources). This chapter focuses instead on emissions from the perspective of the primary types of industrial or physical processes through which sources release most pollutants to the air. The distinction between the major types of releases is not always clear, and the same air toxic can often be released in more than one way from a single source or process. Section 8.2.2 below discusses how the characteristics of these different types of release affect dispersion and transport of air pollutants.

The following terms are routinely used to generally describe or categorize emissions at a facility:

- **Stack or Vent Emissions.** These emissions are how most people envision air pollution. Stacks and vents include “smokestacks” that emit combustion products from fuel or waste combustion, as well as vents that carry air toxics away from people or industrial processes. The major characteristics that stack and vent emissions share are that the release is intentional, they remove airborne materials from specific locations or processes, and they channel the releases through dedicated structures designed specifically for that purpose. Often, stack and vent releases involve the active “pumping” of pollutant-laden air to the external atmosphere by using fans or the “draft” associated with the tendency of hot gases to rise rapidly through cooler, denser air. For many industrial operations, stack and vent emissions account for the bulk of releases (according to the most recent TRI reports from large industrial sources, about 86 percent).⁽¹⁾ For this reason, firms often install pollution control equipment in stacks or vents to reduce the concentration of potentially toxic pollutants released to the environment.
- **Fugitive Emissions.** “Fugitive” emissions are uncontrolled air pollutant releases that “escape” from physical, chemical, or industrial processes and activities, and which do not travel through stacks or vents. Examples include dust or vapors that are generated by the transfer of bulk cargo (e.g., coal, gravel, occasionally organic liquids) from one container to another (e.g., from a tank or hopper car to a storage silo, tank, or bin). Another example includes leaks from joints and valves at industrial facilities and evaporative emissions of fuel from mobile sources.

“Fugitive dust” emissions often occur when quarrying, earth moving, construction, or excavation activities produce particulates. Such emissions are often called “fugitive” because they are uncontrolled (though this is not always the case). Historically, EPA has regarded fugitive emissions as being less important than stack and vent emissions; this is because either the amount of material released was relatively small or the characteristics of the release (large particle size, for example) precluded transport over large distances. However, the combined fugitive emissions from intensive or widespread industrial activities can be as important a contributor to risk as stack emissions.

The following terms are routinely used to describe processes that generate emissions.

- **Particle Suspension and Entrainment.** Particle suspension refers to a set of physical release mechanisms, without reference to specific types of sources and can overlap with the

previous definition of fugitive emissions. Suspension and entrainment refers to any process that results in the release of particles into the air from soils or other surfaces. Suspension and entrainment can occur as a result of artificial soil disturbance; or the action of wind on loose soil, sand or dust. Depending on the nature of the material and atmospheric conditions, suspended particles transport only a few feet, or may transport very long distances before redepositing (for example, dust storms that originate in the Sahara Desert may blow across the Atlantic and impact Central and North America). In some sections of the western United States, the majority of particulate matter detected in air is “crustal material” (soils and fine rock particles) suspended and transported by the wind, rather than human-made pollutants.

- **Volatilization/Vapor Release.** Many organic compounds and some inorganic compounds may “volatilize” to some extent; this means that these compounds tend to evaporate at normal atmospheric temperatures and pressures when not contained. Volatilization can occur for chemicals contained in mixtures as well as from concentrated or pure forms. Common examples include the lighter components of gasoline such as benzene, which volatilize to a sufficient degree that they can be smelled (and sometimes seen) when cars are refueling at filling stations without vapor control systems. Sources can release vapors when handling highly-concentrated or pure organic compounds, as well as when solids and liquids with low levels of organic contamination are exposed to the atmosphere. Volatilization releases are common from chemical manufacturing and processing operations, from metal cleaning and dry cleaning operations that use organic solvents, and from waste management facilities. Volatilization also is important for many natural sources of organic emissions. For example, in heavily forested areas, terpenes (volatile chemicals emitted from pines and other tree species) can account for a large proportions of total organic air pollution.

Common Measures of Chemical Volatility

Henry’s Law Constant. The ratio at equilibrium of the gas phase concentration to the liquid phase concentration of a gas. Note that the Henry’s Law constant can be defined in several ways and expressed using different units.

Vapor pressure. The pressure exerted by a vapor, either by itself or in a mixture of gases; often taken to mean saturated vapor pressure, which is the pressure of a vapor in contact with its liquid form.

Volatile organic compounds (VOCs) are not the only types of substances that vaporize. Some metals (e.g., elemental mercury), organometallic compounds, and other inorganic substances (e.g., ammonia and chlorine) have a high vapor pressure. Many semivolatile organic compounds (SVOCs) also volatilize relatively quickly, albeit at a slower rate than VOCs. Some solids also have a high vapor pressure (mothballs are a common example).

8.2.2 Characteristics of Releases that Affect Dispersion and Transport

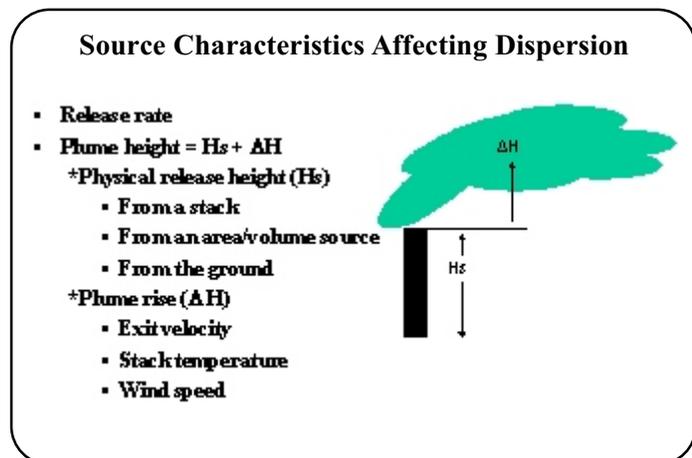
EPA and others have developed several air “dispersion” models to predict the often-complex behavior of air pollution releases. Most air dispersion models take into account a number of characteristics of the source and pollutants released. The most common of these characteristics are described below.

- **Release Rate and Volume.** The rate of release (exit velocity) strongly influences the behavior of the pollutant **plume** as it moves through the atmosphere. In the case of stack and

vent releases, sources can release pollutants as pure vapors, as dilute solutions of vapor in air or other gases, or as suspended particles. Large volumes are often released at a relatively high velocity from stacks or vents, which can also serve to drive pollutants higher in the atmosphere. Air quality models often calculate volume from data on exit area and exit velocity. In the case of fugitive releases or volatilization, the “volume” of release has less meaning, and often does not receive explicit consideration in fate and transport modeling.

- **Concentration.** Concentration (the mass of pollutant per unit volume of released gases) is the other half of the equation that determines the amount (mass) of pollutant released. Pollutants at higher concentrations may also be more likely to condense onto particles or liquid droplets.
- **Temperature.** The temperature of a plume emitted from a stack or vent influences the dispersion and transport of pollutants. A plume that is warmer than the surrounding air will generally rise, which tends to increase the distance over which pollutants will be transported. The combination of temperature and vertical velocity of stack emissions combine to affect the height to which the plume will rise and the layer of the atmosphere in which it will initially be transported. As with concentration, the temperature of the plume also affects the physical form of pollutants, with less volatile pollutants condensing faster from cooler plumes.

- **Height.** Pollutants may also be released into the atmosphere at different heights, and the height of release can strongly affect dispersion and transport. Greater release heights generally result in increased pollutant dilution in the atmosphere, lower ground-level concentrations, and a greater distance to peak ground-level concentrations. Release height also is important in evaluating local effects on air transport, such as building downwash. While power generation or industrial activities may release combustion products from stacks that are hundreds of feet tall, volatilization releases or suspension of particulate pollutants often occur at or near the ground surface.



- **Timing and Duration.** Multiplying the release duration by the release rate produces the total mass of pollutant released. The timing of release relative to specific meteorological conditions determines the particular dispersion and transport of pollutants. Unfortunately, only total annual or average daily release data are available for most sources, making it difficult to fully characterize time varying releases. Fortunately, chronic exposure assessments usually focus on the average long-term (annual) concentrations. Acute exposure assessments, however, usually focus on the maximum short-term (24-hours or less) concentration. Acute exposures are derived from conservative meteorological factors that

lead to the highest short term peak values for a screening exercise; for a more detailed exercise, the actual meteorology should determine the short term peaks.

- **Physical Form.** The physical form of pollutant releases greatly affects the dispersion, transport and chemical reactions that pollutants undergo. Generally, pollutants are characterized as being **vapors** (not bound to particles, but existing as single molecules or very small aggregates “dissolved” in air – also called **gaseous**), **particle-bound** (reversibly absorbed or condensed onto the surface of particles), or **particulate** (irreversibly incorporated into airborne particles). The distribution of pollutants in these three “phases” is known as **partitioning**. Partitioning is a function of the chemical and physical properties of the pollutants and the temperature and pressure of the atmosphere into which the chemicals have been released (e.g., the partitioning behavior of pollutants can vary greatly with temperature). As noted above, sources can emit chemical pollutants in the vapor phase at relatively high temperatures, and these pollutants can condense into or onto particulates as the emitted gases cool in the atmosphere. Sources generally emit most metals (with the important exception of mercury) as particles in the atmosphere.
- **Particle Size.** When sources release pollutants as particles (or if released as gases, if these pollutants condense into particles or absorb onto the surface of existing particles), the rate of pollutant removal from the atmosphere to surfaces (e.g., plants, soils, surface water) depends upon particle size. The typical size of particles that different activities and processes emit into the air can vary by many orders of magnitude (powers of ten). As the size of particles increases, the rate at which particles fall due to gravity (the settling velocity) increases. Thus, fine particles (approximate diameter less than a few microns)^(a) may remain suspended in air indefinitely, but particles larger than about 20 microns in diameter settle rapidly and may not transport far from sources of release.

For purposes of air toxics risk assessment, particles less than 10 microns in diameter are of primary concern because they are small enough to be taken into and deposited in the lung after inhalation. These particles are divided into two size ranges: “fine” particles less than 2.5 micrometers in size ($PM_{2.5}$), and “coarse” particles covering the range from 2.5 to 10 micrometers in diameter (PM_{10}). (Thus, monitoring analyses for metals in particulates, for example, would commonly collect particulate samples of $PM_{2.5}$ and PM_{10} for analysis, not total suspended particulate (TSP), because such samples contain particles that are too large to be effectively respired – thereby leading assessors to overestimate inhalation risk).

Particles emitted from combustion and high-temperature chemical processes can be very fine, on the order of 0.01 to 1.0 microns in diameter. Such fine particles tend to condense to form larger aggregates up to the limit of perhaps a few microns, and participate in a wide range of chemical reactions.

^aOne micron is one one-millionth of a meter, or about 0.00004 inches.

Aerosols and Particulate Matter

Aerosols are mixtures of fine solid or liquid particles in a gas. They can be emitted directly as particles or formed in the atmosphere by gas-to-particle conversion processes. The terms dust, smoke, fume, haze, and mist all describe different types of aerosols. Dust refers to solid particles produced by disintegration process; smoke and fume are particles formed from the gas phase. Mists are composed of liquid droplets. Some aerosols occur naturally, originating from volcanoes, dust storms, forest and grassland fires, living vegetation, and sea spray. Human activities, such as the burning of fossil fuels and the alteration of natural surface cover, also generate aerosols.

Particulate matter is the term given to the tiny particles of solid or semi-solid material found in the atmosphere. Particulates less than about 50 micrometers in size are called total suspended particulates (TSP). Particles larger than that range tend to quickly settle out of the air. Particulate matter 10 micrometers in diameter and smaller (PM_{10}) is considered inhalable. These particles are divided into two size ranges: fine and coarse.

“Fine” particles less than 2.5 micrometers in size ($PM_{2.5}$) are responsible for causing the greatest harm to human health. 1/20th the width of a human hair, these fine particles can be inhaled deep into the lungs, reaching areas where the cells replenish the blood with oxygen. They can cause breathing and respiratory symptoms, irritation, inflammation, damage to the lungs, and premature deaths. Some $PM_{2.5}$ are released directly to the atmosphere from industrial smokestacks and automobile exhaust, but a large percentage is actually formed in the atmosphere from other pollutants such as sulphur dioxide, nitrogen oxides, and volatile organic compounds.

“Coarse” particles covering the range from 2.5 to 10 micrometers in diameter are also known to cause adverse health effects, such as aggravation of respiratory disease. When inhaled, particles larger than 10 micrometers tend to be deposited in the upper parts of the respiratory system, from which they can be eventually expelled back into the throat. Coarse particles generally remain in the form in which they are released into the atmosphere without chemical transformation, eventually settling out under the influence of gravity. While some of these coarse particles are generated naturally by sea salt spray, wind and wave erosion, volcanic dust, windblown soil, and pollen, they are also produced by human activities, such as construction, demolition, mining, road dust, tire wear, and grinding processes of soil, rocks, or metals.

- **Chemical Form.** Chemical form is generally more of a concern for inorganic pollutants, because organic chemicals tend to have well-defined chemical compositions and properties. The most important chemical properties of inorganic metal compounds, for example, include the **oxidation** or **valence state** of the **cationic metal**, the identity of the **anionic counterion**, and the chemical and physical properties of the compound that the cation and anion comprise. As an example of the importance of valence state, consider the metal chromium. When emitted in the *hexavalent* form (with six positive charges – Cr^{6+}), chromium is highly reactive chemically and is readily reduced under certain conditions to the *trivalent* form, which is Cr^{3+} . Cr^{6+} can cause respiratory irritation and cancer in humans. Cr^{3+} , on the other hand, is much more stable, is much less toxic to humans and animals (and is actually an essential mineral), and is not thought to cause cancer.

Available air pollution dispersion models differ in the ways in which they use these characteristics. While Chapter 9 presents a general discussion of these, users can find specific details in the documentation for the various models at EPA's (Support Center for Regulatory Air Models) SCRAM website.⁽²⁾

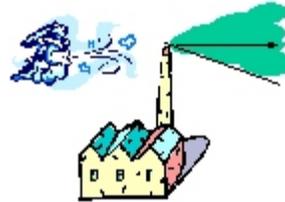
8.2.3 Physical and Meteorological Factors Affecting Air Toxics Dispersion and Transport

This section describes some of the most important physical and meteorological factors that affect the movement of air pollutants after their release. For definitions of and further details about the atmospheric and meteorological terms this section uses, refer to Appendix G.

Although this section focuses on releases from stationary point sources (i.e., stacks), most of the factors may apply to releases from other source types as well. Stacks come in all sizes, from a small vent on a roof to stacks hundreds of feet in height. The function of a stack is to remove pollution of high concentration and to discharge it to the atmosphere for dispersion and transport. Stacks release pollutants high enough above the earth's surface that pollutants can sufficiently disperse in the atmosphere before reaching ground level. All else being equal, taller stacks disperse pollutants more effectively than shorter stacks because the pollutants release into higher wind speeds and travel through a greater depth of the atmosphere before reaching ground level.

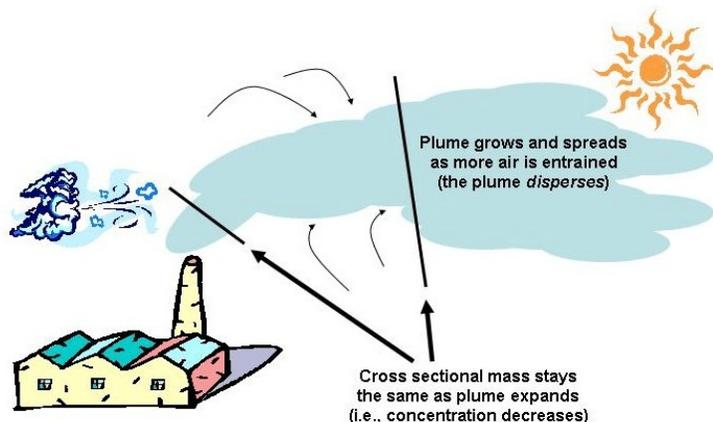
The air space the stack pollutant occupies can be described as a **plume**. As the plume travels, it spreads and disperses, reducing ambient pollutant concentrations even though the cross sectional mass of the plume remains the same. Eventually, the plume may intercept the ground. The combination of emission velocity, emission temperature (see below), vertical air movement and horizontal airflow all influences how high a plume will rise and how fast and far it travels. Another factor is wind meander (i.e., changes in wind direction during light wind speed

Wind Speed and Direction Affect Plume Dispersion



The wind will determine which direction the plume goes and how fast it gets there. To look at long-term impacts (chronic exposure) a wind-rose (a distribution of winds around a compass) can be used to determine the areas of persistent wind; downwind of the largest persistent winds will generally be the areas to expect the maximum long-term impacts.

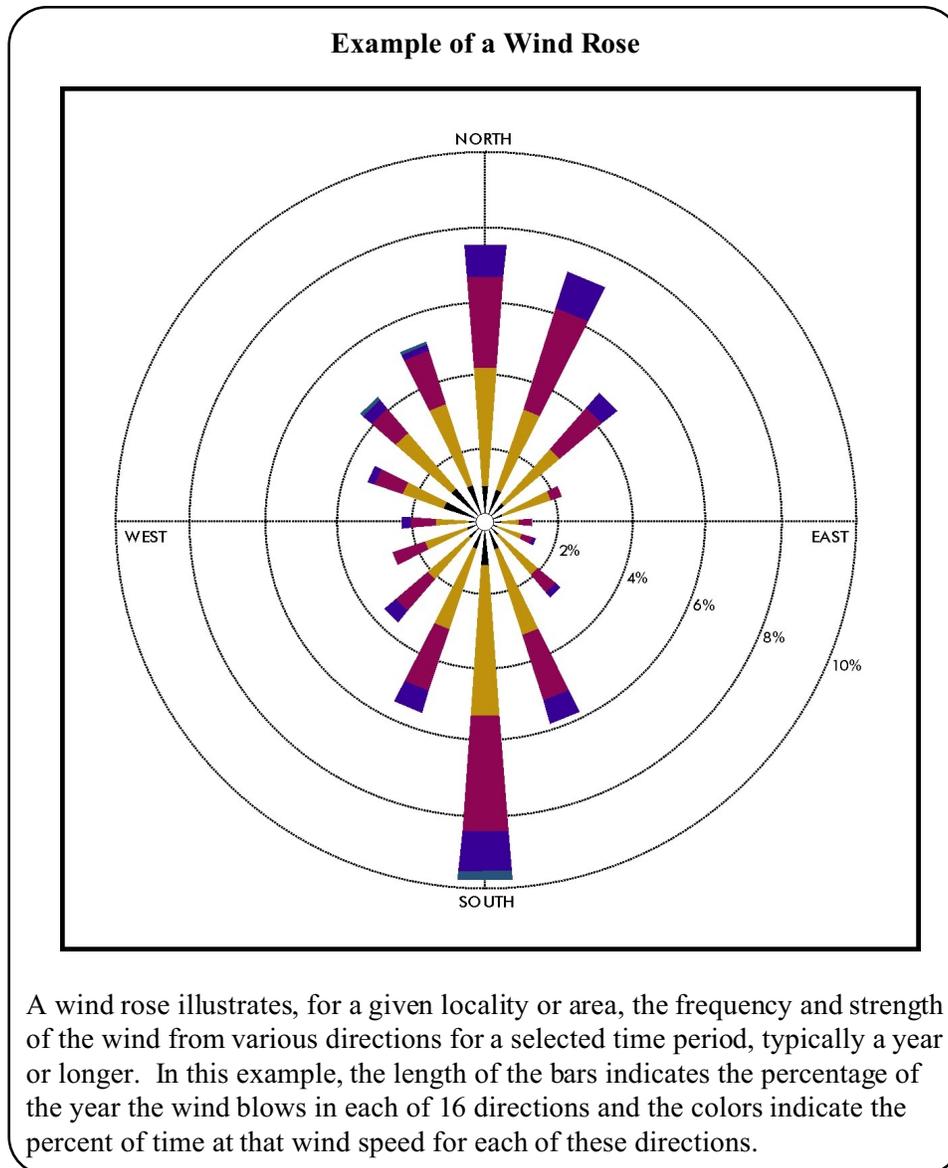
Concentrations of Air Toxics in a Plume Decrease With Distance



As a plume grows, it entrains clean ambient air and disperses. In other words, the amount of pollutant mass at any given cross section in the plume is generally the same; thus, as the plume spreads, its concentration goes down.

conditions), which can cause the plume to deviate in the horizontal direction due to turbulence and wind fluctuation.

As the gases exit the stack, they mix with ambient air. This mixing of ambient air into the plume is called **entrainment**. The plume grows in volume as it entrains ambient air and travels downwind. Because stack gases are often warmer than the ambient outdoor air, the gases may be less dense and than the outdoor air and are therefore buoyant (like a helium filled balloon). Gases that stacks emit are often pushed out by fans giving the gas momentum as it enters the atmosphere. The combination of this momentum and the buoyancy of the stack gases that are warmer than the ambient air cause the gas to rise.



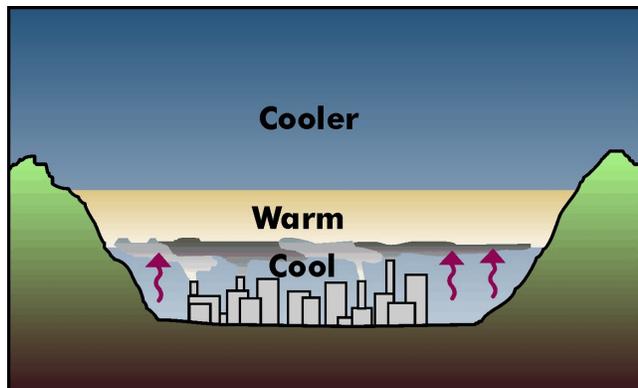
This plume rise allows air toxics emitted in this stack stream to be lofted higher in the atmosphere. Since the plume is higher in the atmosphere where the winds are generally stronger, the plume will generally disperse more before it reaches ground level. Plume rise depends on the stack's physical characteristics and on the effluent's exit temperature and velocity.

Vertical Air Motions

When air is displaced vertically, atmospheric behavior is a function of atmospheric stability. A stable atmosphere resists vertical motion, and air that is displaced vertically in a stable atmosphere tends to return to its original position. This atmospheric characteristic determines the ability of the atmosphere to disperse pollutants. To understand atmospheric stability and the role it plays in pollution dispersion, it is important to understand the dynamics of the atmosphere as they relate to vertical atmospheric motion.

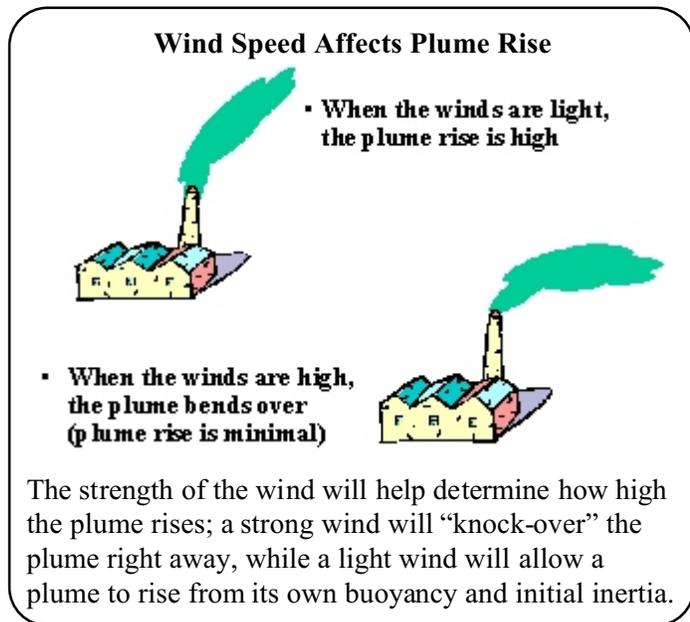
The degree of stability of the atmosphere is determined by the temperature difference between an air parcel and the surrounding air. This difference can cause the parcel to rise or fall. There are three general categories of atmospheric stability.

- In **stable** conditions, vertical movement tends not to occur. Stable conditions occur at night when there is little or no wind. Air that lifts vertically will remain cooler, and therefore denser than the surrounding air. Once the lifting force ceases, the air that has lifted will return to its original position.
- **Neutral** conditions (“well mixed”) neither encourage nor discourage air movement. Neutral stability occurs on windy days or when there is cloud cover such that there is neither strong heating nor cooling of the earth’s surface. Air lifted vertically will tend to remain at the higher level once the lifting force ceases.
- In **unstable** conditions, the air parcel tends to move upward or downward and to continue that movement. Unstable conditions most commonly develop on sunny days with low wind speeds where strong solar radiation is present. The earth rapidly absorbs heat and transfers some of it to the surface air layer. As warm air rises, cooler air moves underneath. The cooler air, in turn, may be heated by the earth’s surface and begin to rise. Such conditions enhance vertical motion in both directions and considerable vertical mixing occurs.
- **Inversions** occur whenever warm air overruns cold air and “traps” the cold air beneath. Within these inversions there is little air motion, and the air becomes stagnant. High air toxic concentrations can occur within inversions due to the limited amount of mixing between the “trapped” air and the surrounding atmosphere. Inversions can limit the volume of air into which emissions are dispersed, even from tall stacks.



The condition of the atmosphere (i.e., the vertical profile of the winds and temperature) along the path of the plume also determines how far the plume rises in the atmosphere. As described in Appendix G an **inversion layer** (formed when a layer of warm air “traps” a layer of cold air beneath) may act as a barrier to vertical mixing. The height of a stack in relation to the height of the inversion layer may often influence ground-level pollutant concentrations (Exhibit 8-1).

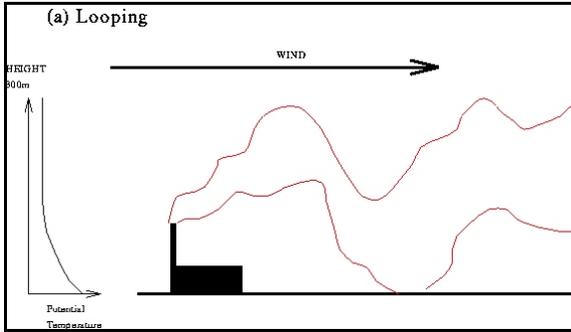
The initial velocity of the plume (stack exit velocity) reduces quickly as the plume entrains ambient air and acquires horizontal momentum from the wind. This momentum causes the plume to bend over. The greater the wind speed, the more horizontal momentum the plume acquires. Wind speed usually increases with height above the earth’s surface. Therefore, as the plume continues upward the stronger winds tilt the plume even further. This process continues until the plume may appear to be horizontal to the ground. The point where the plume looks level may be a considerable distance downwind from the stack (Exhibit 8-2).



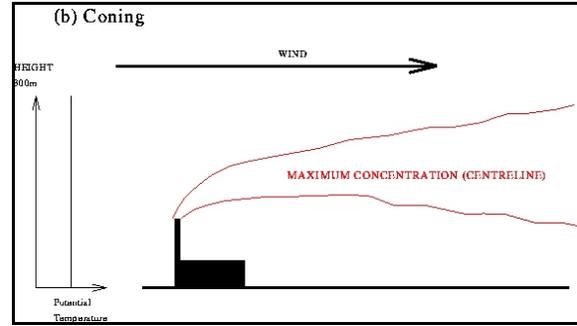
Due to configuration of the stack or adjacent buildings, the plume may not rise freely into the atmosphere. The way in which the wind moves around adjacent buildings and the stack can force the plume toward the ground instead of allowing it to rise in the atmosphere. Stack-tip downwash can occur where the ratio of the stack exit velocity to horizontal wind speed is small. In this case, low pressure in the wake of the stack may cause the plume to draw downward behind the stack. Pollutant plume rise reduces when this occurs and elevates pollutant concentrations immediately downwind of the source. As air moves over and around buildings and other structures, it forms turbulent wakes. Depending upon the stack height, it may be possible for the plume to be pulled down into this wake area. The reduction in plume height is known as **aerodynamic or building downwash** (Exhibit 8-3).

Once air toxics have equilibrated with ambient conditions (e.g., temperature, velocity), atmospheric and meteorologic factors primarily influence dispersion and transport of air toxics. In particular, the rate of dispersion is influenced by both the thermal structure of the atmosphere and mechanical agitation of the air as it moves over the different surface features of the earth (see Appendix G). As the next section describes, exposure to solar radiation and moisture, as well as other properties in the atmosphere, complement the factors above and contribute to the eventual fate of the air toxics.

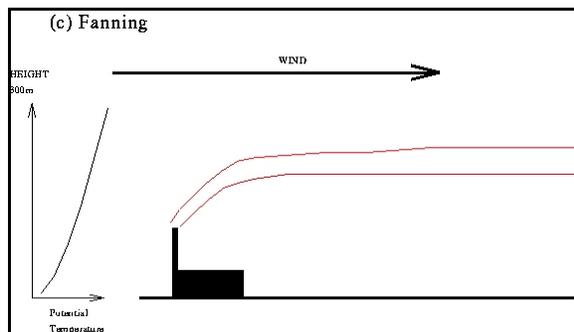
Exhibit 8-1. Effects of Boundary Layer Conditions on Plume Dispersion



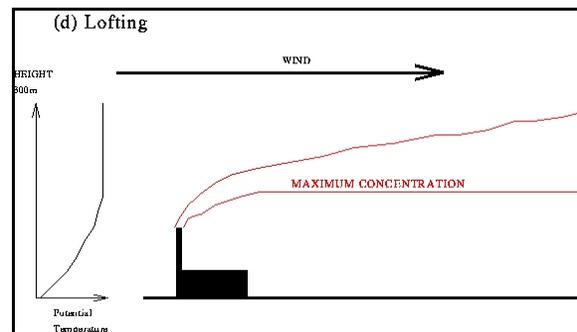
(a) Looping. When the atmosphere is very unstable through a deep layer, convective currents carry the plume up and down, forming a looping pattern and rapidly diluting the plume through intense vertical mixing.



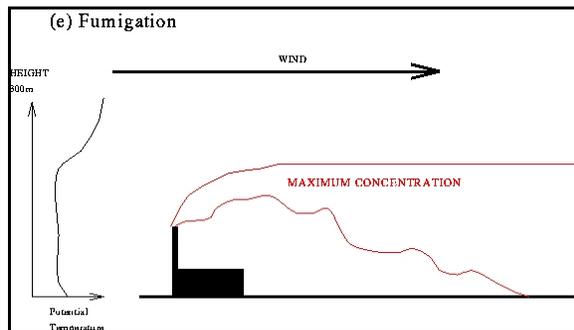
(b) Coning. Under neutral conditions, the vertical mixing also transports freely, but the turbulent motions that irregularities of the ground and shearing of the wind introduce are about equal, and the plume resembles a cone.



(c) Fanning. When the plume rises into an inversion layer, the stability limits diffusion up or down, so that the only spreading of the plume is sideways and when viewed from above has a fanning appearance.



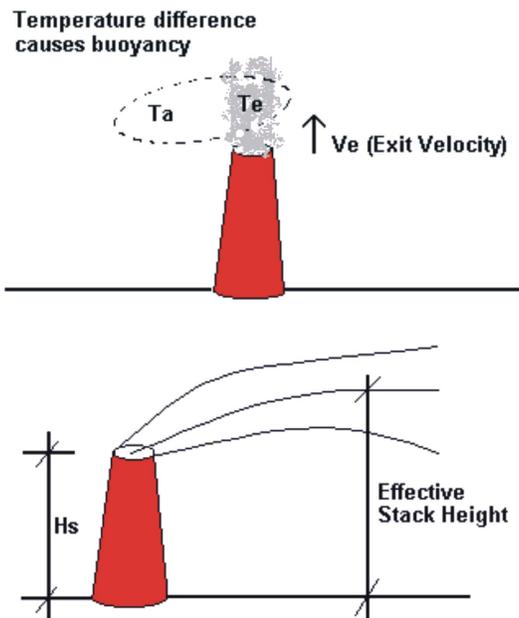
(d) Lofting. When conditions are unstable or neutral above an inversion, the release of a plume above the inversion is more likely to result in effective dispersion and lower ground-level concentrations around the source



(e) Fumigation. If the plume is released overnight just under an inversion layer, it can become trapped. As solar radiation warms the ground in the morning, the air below an inversion layer becomes unstable. If the unstable conditions then extend upwards and reach the plume that is still trapped below the inversion layer, the pollutants can be rapidly transported down toward the ground. Ground-level pollutant concentrations can be very high when fumigation occurs.

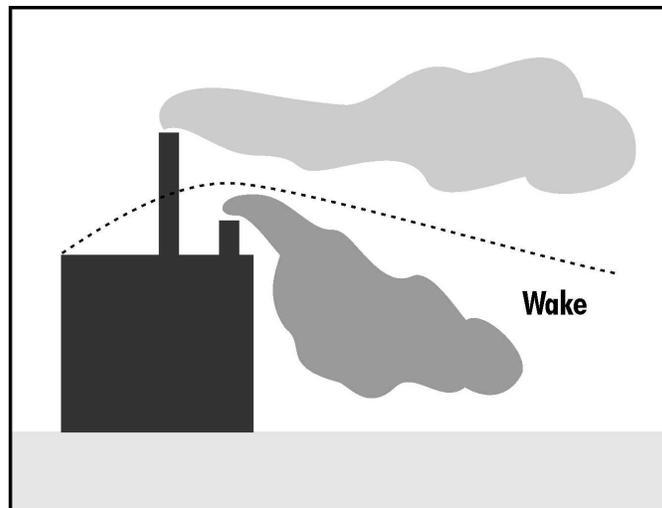
Graphics courtesy of Doug Parker, University of Leeds, and available at: <http://www.env.leeds.ac.uk/envi1250/lectures/lect11.html>.

Exhibit 8-2. Plume Rise Schematic



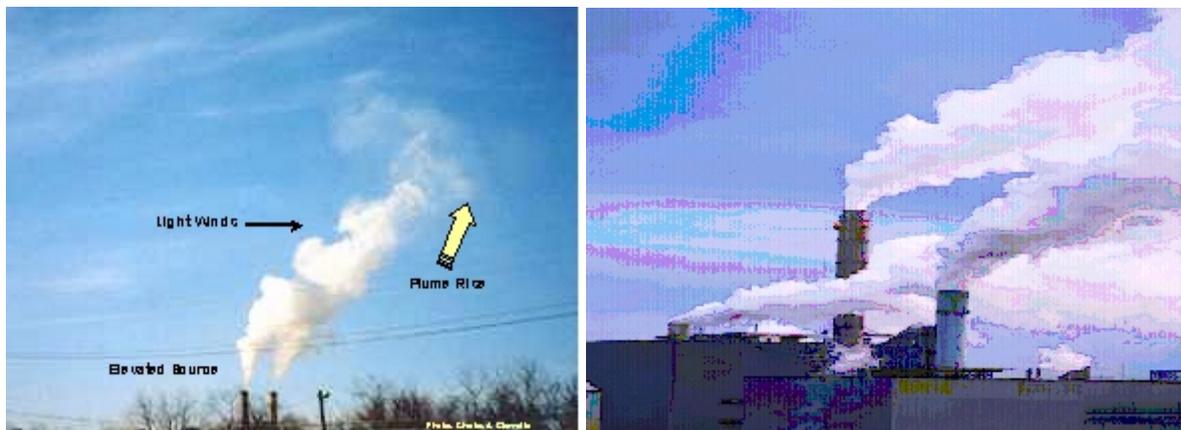
As emissions exit a stack, they can be lofted higher into the atmosphere as a result of plume rise. Plume rise is caused by (1) buoyancy resulting from emissions with higher temperatures than ambient air (i.e., $T_e > T_a$) and (2) the initial momentum (i.e., exit velocity) of the emissions leaving the stack. The effective stack height of a stack is equal to the actual physical height of the top of the stack (H_s) plus the plume rise, minus any downwash associated with wake turbulence behind objects on the ground (see Exhibit 8-3).

Exhibit 8-3. Aerodynamic or Building Downwash



Nearby structures can disturb the horizontal flow of the wind (indicated by the dashed line) and cause a plume to get “downwashed” to the ground quickly. This is how a snow fence works.

Examples of Plume Rise



The picture on the left is an example of an elevated point source that probably has a hot plume or high exit velocity, as the plume rise indicates. Because of the light wind and neutral or unstable atmospheric conditions, there are essentially no impacts at ground level near the source. The picture on the right is another example of elevated point sources, but this time with higher winds. There is little plume rise, and the plumes fan straighter out from the stacks, resulting in narrower plumes.

8.3 Fate of Air Toxics in the Atmosphere

This section discusses the major physical and chemical processes that affect the fate of air toxics in the atmosphere. The scope of this section is limited to processes that remove air toxics from the atmosphere. Part III of this reference manual discusses the fate and transport of air toxics in other environmental media and the ecosystem once a chemical has been removed from the air.

8.3.1 Physical Processes Removing Air Toxics

A number of important physical processes (processes that do not alter the chemical nature of pollutants) affect how air toxics move in and out of the atmosphere. In particular, this section discusses how gravity and precipitation remove air toxics from the atmosphere. The process through which particulates fall (or settle) to the surface in the absence of precipitation is known as **dry deposition**, and the removal of pollutants from the air through precipitation events is called **wet deposition**.

- **Dry Deposition.** As the previous section noted, dry deposition is the settling of particles due to gravity. The maximum speed at which a particle will fall in still air is known as the **settling velocity (settling rate)**. A particle's settling velocity is a function of its size, density, and shape. Larger, denser particles settle more rapidly, and particles with more irregular shape settle more slowly (Exhibit 8-4). For particles smaller than a few microns in diameter (fine and ultrafine particles), the gravitational settling rate is so slow that other forces, such as local air currents and collisions with gas molecules, tend to offset it. Thus, in the absence of other removal mechanisms (e.g., condensation and/or aggregation to form larger particles, wet deposition), particles in this size range tend to remain suspended in the

air for long periods of time. Depending on the conditions, fine particles may persist in the atmosphere for days or weeks and travel hundreds or thousands of miles from their source. At the other extreme, coarse dust particles (> 50 microns in diameter), such as those generated while handling materials, have large settling velocities. Under normal conditions, such particles generated near the ground will deposit on the surface within a few seconds or minutes, generally within less than a kilometer of the source. Particles in between these two extremes in the size distribution will settle at intermediate velocities, and will distribute at intermediate distances from their sources.

Exhibit 8-4. Approximate Settling Rates for Typical Particles in Air	
Equivalent Diameter* (microns)	Settling Rate (cm/sec)
0.01	0.00001
0.1	0.0002
1.0	0.01
10	0.6
100	40

* Diameter of a sphere that is approximately equivalent to a particle's diameter

In typical air dispersion models, the modeler must specify a particle size distribution, classifying what proportion of the emitted particles are within particular size ranges. In initial screening-level analyses of pollutant levels in air, users assume that particulate settling does not occur. This is conservative relative to the air concentration - if the amount deposited to the ground is the key issue of concern, then a high removal rate from the atmosphere would be “conservative.” Users can assess dry deposition for low-volatility pollutants that partition out of the air primarily onto airborne particles in the same fashion as non-volatile particulates. Volatile chemicals that exist primarily in the vapor phase have negligible settling velocities, and modelers generally need not consider dry deposition for these pollutants. In the case of pollutants whose vapor-particle partitioning is unclear, it is common to run air dispersion models assuming a range of partitioning behavior from fully particle-bound to fully vapor phase.

- Wet Deposition.** Wet deposition involves the “washing out” of pollutants from the atmosphere through precipitation events (including rain, snow, and in some cases hail). Wet deposition affects both particulate and vapor-phase pollutants. For larger particles and vapor phase pollutants that are soluble in water, precipitation is very efficient at removing pollutants from the air and depositing them on the earth’s surface. Wet deposition may be less efficient at removing fine particulates, and has limited effect on the levels of gaseous pollutants with high Henry’s Law constants (indicating low solubility in water compared to vapor pressure). Because wet deposition depends on the occurrence of precipitation events, it is best characterized over long periods (e.g., seasons or years). The relative importance of precipitation in removing pollutants from the air depends on the climatic conditions in the areas affected by pollution.

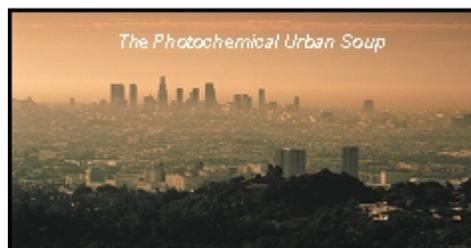
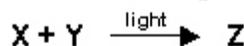
Transport and Deposition of Mercury

Mercury is a natural trace element in nearly all coal, and the large quantities burned in major electric power plants can release considerable mercury. In both municipal and medical incinerators the variety of waste materials burned can include mercury. Some mercury remains in the ash-materials, some may be captured by pollution controls on exhaust, and the rest is emitted to the air in three forms or chemical “species:” gaseous elemental mercury (Hg(0)), gaseous ionic or “inorganic” mercury (Hg(II)), and particle-bound mercury (Hg(p)). Elemental mercury gas is nearly insoluble in water and rather inert chemically, so it can be transported up to thousands of miles while gradually being converted to other forms and deposited. The ionic form, Hg(II) or Hg (2+), is soluble in water and thus incorporated into rain, fog, and snow. Also, Hg(II) is both physically and chemically active and is known as “reactive gaseous mercury” or RGM. Most of the Hg(II) emitted is deposited via both precipitation and dry gases within about 30 to 60 miles from a stack. In many cases, this “local” deposition can be the most important impact of mercury from combustion sources. The fate of particle-bound mercury depends on the size of the particles, though generally they deposit to earth within a few hundred miles of the emitting stack.

8.3.2 Chemical Reactions that Remove Air Toxics

In addition to deposition, chemical reactions may occur that reduce air toxics concentrations. Air toxics may be destroyed through the action of sunlight, through reactions with atmospheric chemical pollutants, or through a combination of these pathways. In estimating the ambient air concentration associated with air toxics releases, it is therefore necessary to consider chemical reactions as well as deposition. As will be discussed in the next section, not all chemical reactions result in the destruction of air toxics, or their conversion to less harmful products. Potentially harmful pollutants may also be formed as a result of atmospheric chemical reactions (a process that is called **secondary production** or **secondary formation**). This section, however, focuses on atmospheric chemical reactions which are known or believed to destroy air toxics (i.e., resulting in less toxic forms).

Chemical Transformations Can Occur in the Atmosphere



Numerous complex chemical transformations may occur in the atmosphere, some of which are photochemical in nature (i.e., reactions in the presence of light to form new chemicals).

- **Major Chemical Reactions of Air Toxics.** Generally, organic compounds are much more susceptible to chemical reactions in the atmosphere than metals or other inorganic contaminants. The major chemical reactions undergone by organic chemicals in the atmosphere include:
 - Photolysis (destruction by sunlight alone);
 - Reactions with the hydroxyl radical (OH•);

- Reactions with the nitrate radical (NO₃•); and
- Reaction with ozone (O₃).

Often these reactions occur in combination with reactions that are strongly affected by sunlight. While reaction rates vary widely for pollutants, under typical atmospheric conditions, reactions with the hydroxyl radical are the most rapid, and account for a large portion of pollutant degradation during daylight hours. Reactions with nitrate radical occur primarily during the night, and reactions with ozone occur both day and night. Except in the case of a few pollutants, “pure” photolysis is a relatively minor reaction process. Other reactive species such as the hydroperoxide radical (OOH•) may also participate in pollutant degrading reactions under some conditions. The relative importance of these reactions is dependent not only on climatic factors (e.g., duration and intensity of sunlight), but also on the overall concentrations of pollution present. For example, high levels of nitrogen oxide (NO_x) emissions and emissions of VOCs increase the levels of nitrate radicals and ozone in the atmosphere, thereby increasing reaction rates for subsequent reactions where these species are involved.

8.3.3 Chemical Reactions that Result in the Secondary Formation of Pollutants

As noted previously, not all chemical reactions result in the destruction of pollutants or in reaction products that are of less concern than the pollutants from which they derive. In some cases, the immediate reaction products result in products that are more toxic and/or more persistent than the chemicals that were originally released into the atmosphere.

Examples of large-scale chemical reactions that result in products that can be hazardous to health include the generation of acid particulate through photo-oxidation after the release of sulfur dioxide (SO₂) and NO_x from combustion sources (i.e., to make sulfuric acid and nitric acid), and the formation of ozone and photochemical oxidant in areas with high levels of NO_x and volatile organic emissions. In addition, there are many reactions of specific organic pollutants that generate air toxics of concern, as Exhibit 8-5 shows. The extent to

Exhibit 8-5. Examples of Secondary Pollutants	
Pollutant	Formed From
acetaldehyde	propene, 2-butene
acrolein	1,3-butadiene
carbonyl sulfide	carbon disulfide
o-cresol	toluene
formaldehyde	ethene, propene
hydrogen chloride	nitric acid, chlorinated organics
methylethyl ketone	butane, branched alkenes
N-nitroso-N-methylurea	N-methylurea
N-nitrosodiethylamine	dimethylamine
N-nitrosomorpholine	morpholine
phosgene	chlorinated solvents
propionaldehyde	1-butene
Source: Rosenbaum et al., 1998 ⁽³⁾	

which these reactions are important at any given location depend, of course, on the emissions and resulting concentrations of the precursor materials. In addition, many of these reactions are catalyzed directly and indirectly by sunlight, so weather and climatic factors are important in judging the importance of secondary formation. While it is difficult to generalize, the secondary formation of formaldehyde and acrolein are thought to be important in many regions of the country with significant industrial and mobile source emissions.⁽³⁾

8.3.4 Overall Persistence of Air Toxics in the Atmosphere

In analyzing the potential impacts of air toxics releases, it is necessary to combine considerations of all the above processes to characterize the overall pattern of air toxics concentrations and estimate the time periods and distance scales over which air toxics impacts need to be evaluated.

Detailed quantitative comparisons of removal pathways may be too complex and expensive to include in most risk assessments. However, air pollution scientists have developed a number of simple models and gathered data on a large number of pollutants that enable them to assess the relative impacts of different physical processes and chemical reactions on single chemicals under typical conditions. The most common model uses the simplifying assumption that pollutant removal through each chemical and physical processes can be approximated using processes that have characteristic **half-lives** and **atmospheric lifetimes** (Exhibit 8-6).

Under the most commonly used approach (many variations exist), the overall lifetime of a pollutant in the environment is:

$$\frac{1}{r_{\text{overall}}} = \frac{1}{r_{\text{physical}}} + \frac{1}{r_{\text{chemical}}} \quad (\text{Equation 8-1})$$

That is, the overall lifetime ($1/r_{\text{overall}}$) of a chemical in the environment is equal to the sum of the atmospheric lifetime when considering only physical processes ($1/r_{\text{physical}}$) plus the lifetime when considering only chemical processes ($1/r_{\text{chemical}}$). This equation is the same as saying that the overall rate constant for pollutant removal/destruction (r_{overall}) is equal to the sum of the rate constant for physical removal (r_{physical}) plus the rate constant for chemical reaction ($1/r_{\text{chemical}}$). This relationship follows from the nature of first-order reaction kinetics, and is known to be only an approximate description of actual physical processes (see Exhibit 8-5). It is a useful approximation, however, that can be used to evaluate the importance of atmospheric processes for many pollutants.

As noted in Section 8.2.2, organic chemical pollutants can undergo a number of chemical reactions that may be important under different sets of conditions. Thus, the atmospheric lifetime for chemical reactions in the above equation is often broken down to consider contributions from each important reaction:

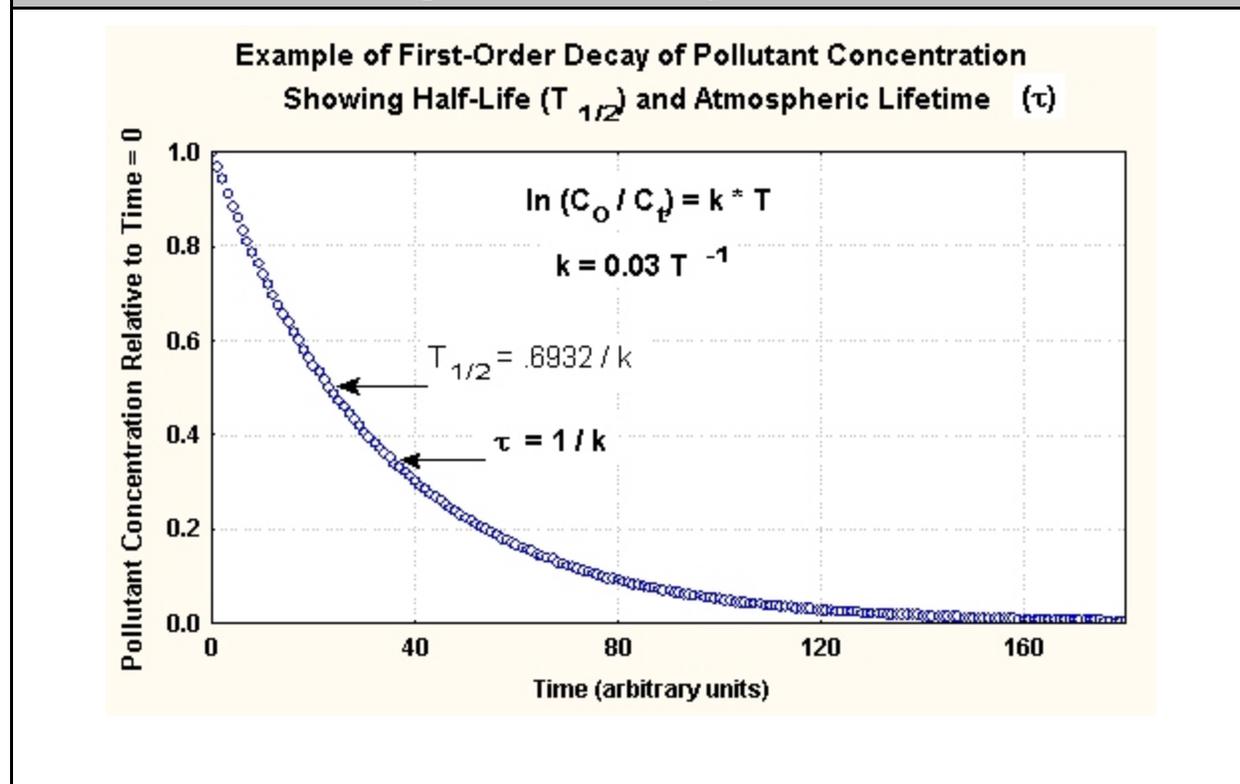
$$\frac{1}{r_{\text{chemical}}} = \frac{1}{r_{\text{OH}}} + \frac{1}{r_{\text{NO}_3}} + \frac{1}{r_{\text{O}_3}} + \frac{1}{r_{\text{photolysis}}} \quad (\text{Equation 8-2})$$

where the terms on the right side of the equations represent the rates of pollutant removal through the reactions with hydroxide radical, nitrate radical, ozone, and photolysis, respectively.

For any given air toxic, overall persistence in the atmosphere depends on particle-vapor partitioning behavior, particle size distribution (if the material is non-volatile), and susceptibility

to various types of chemical reactions. Atmospheric half-lives due to deposition (wet and dry) tend to be highly variable depending on particle size, ranging from a few minutes for coarse particles to many days for very fine particles. Most fine particles (less than a few microns) are removed from the troposphere (the lower level of the atmosphere where most weather takes place) with an average lifetime of between 5 and 15 days.

Exhibit 8-6. Example First-Order Decay of Pollutant Concentration



Simple physical and chemical reactions often proceed according to what are called “first-order kinetics.” In a first-order reaction, the rate of the reaction at any given time is proportional to the concentration of one reactant (in this case, the air toxic that is being destroyed). The overall rate of the reaction is governed by the first-order (or “pseudo first-order”) rate constant, “k.” A higher rate constant implies a higher reaction rate for a given concentration of reactant. First-order reactions have the properties that the “half-life” of the reaction (the time in which one-half of the original concentration of reactant is destroyed) is the same no matter what the initial concentration. Air pollution scientists also measure the “atmospheric lifetime” of pollutants, which is abbreviated as the Greek letter τ (tau) or the letter “r,” which is equal to $1/k$. In this example, the rate constant (k) represents the sum of both physical and chemical removal.

Exhibit 8-7 presents estimated *chemical* half-lives for a few example chemicals based on measured reaction rates. Estimated atmospheric lifetime for chemical reactions ranges from many thousands of hours for the least reactive chemicals to only a few hours for chemicals that are more reactive. As noted above, the lifetimes for reactions with the hydroxide radical (r_{OH}) are the shortest, indicating that this pathway is the most important for most of the chemicals in the table, at least during daylight hours. Reactions with ozone and nitrate radicals are much slower

for most of the chemicals. “Pure” photolysis is not important for most chemicals, with the notable exceptions of the two aldehydes, where it is a major degradation pathway.⁽⁴⁾

Exhibit 8-7. Typical Atmospheric Half-lives for Chemical Reactions (hours) for Selected Pollutants for Reactions with Hydroxide, Nitrate, Ozone, and for Photolysis				
Compound	r_{OH}	r_{O₃}	r_{NO₃}	r_{photolysis}
methane	28,000	2x10 ⁸	2x10 ⁶	–
ethane	8,40	3x10 ⁷	1x10 ⁵	–
benzene	180	4x10 ⁶	4x10 ⁶	–
toluene	37	3x10 ⁵	3x10 ⁵	–
1-butene	7.4	26	93	–
isoprene	2.3	20	1.4	–
formaldehyde	19	–	–	5.5
acetaldehyde	12	5,600	–	2.7

Source: California Air Resources Board Toxic Air Contaminant Fact Sheets⁽⁴⁾

Data such as those in Exhibit 8-7 are available to some degree for many chemicals, and can help assessors to judge the distance scales over which to analyze air toxics impacts. As noted above, persistence on the order of less than a day suggests transport of about ten miles, while persistence for several days suggests regional transport (500-1,000 miles) before being substantially degraded. Atmospheric reactivity is not well-studied for some chemicals, requiring the use of assumptions about persistence that span a reasonable range of reactivity. For non-volatile air toxics that partition primarily into particles, physical processes (wet and dry deposition) may be the most important in determining overall atmospheric lifetimes.⁽⁴⁾ Some chemicals that are very persistent in the atmosphere and in terrestrial and aquatic systems may require special consideration, as described in Chapter 17. Chapter 9 builds upon the discussion above and identifies how well available dispersion models address chemistry/physical removal.

References

1. U.S. Environmental Protection Agency. 2003. 2001 Toxics Release Inventory (TRI) Public Data Release Report. Office of Environmental Information, Washington, D.C., July. Available at: <http://www.epa.gov/tri/tridata/tri01/index.htm>.
2. U.S. Environmental Protection Agency. 2004. Technology Transfer Network. *Support Center for Regulatory Air Models*. Updated February 23, 2004. Available at: <http://www.epa.gov/ttn/scram/>. (Last accessed March 2004).
3. Rosenbaum, A.S., Ligoeki, M.P., and Wei, Y.H. 1998. *Modeling Cumulative Outdoor Concentrations of Hazardous Air Pollutants, Volume 1: Text*. SYSAPP-99-96/33r2, Prepared for U.S. Environmental Protection Agency, Office of Policy, Planning and Evaluation, by Systems Applications International, Inc., San Rafael, CA.
4. California Air Resources Board. 1998. *Toxic Air Contaminant Fact Sheets*. Available at: <http://www.arb.ca.gov/toxics/tac/tac.htm>. (Last accessed March 2004).