Ask most people what they regard as the defining characteristic of the urban atmosphere and they refer to its degraded air quality: the distinct odour, reduced visibility or irritating effects in the throat or eyes. Inevitably, the concentration of human activities in cities results in emissions that modify the thermal and chemical composition of the urban atmosphere.

Figure 11.1 illustrates the experience of urban living for many; a busy street in Cairo, Egypt, crowds intermingle with cars, buses and motorbikes, each of which injects heat, moisture, noise and a host of air pollutants into the urban canopy layer (UCL). All of this occurs within a street canyon that confines the air flow and restricts the dilution of air pollutants. Contaminated air drifts into adjacent buildings where it lingers longer and affects the comfort and health of occupants. Although air pollution is not confined to cities, the density and complex intermingling of emission sources, their proximity to large populations coupled with distinct features of urban meteorology (such as recirculating flows in streets), means it has particular relevance there.

This chapter introduces the topic of air pollution meteorology and climatology as it applies to urban areas. Further, it deals with the resulting effects of urban pollutant emissions on air quality at regional to continental scale. It is a subject with an extensive and lengthy history, much of which overlaps with the broader subject of urban climatology. In particular there are special connections to questions of airflow (Chapter 4) and temperature structure (Chapter 7) because urban air pollution depends critically on wind, turbulence and stability that operate across the spectrum of urban scales to transport, dilute and
ultimately remove urban pollutants. We begin as before with a discussion of the basics of air pollution before considering its urban character: readers experienced with the chemical and physical fundamentals of air pollution can skip to Section 11.2.

### 11.1 Basics of Air Pollution

Air pollutants are substances which, when present in the atmosphere in sufficient concentration, may harm human, animal, plant or microbial health, or damage infrastructure or ecosystems. The most common air pollutants found in urban air are listed in Table 11.1 along with their potential impacts on human health and ecosystems. Air pollutants occur in all states (gaseous, dissolved in droplets, liquid or solid particulates). In all cases, they are transported by the air flow and mixed by turbulence.

Air pollution is the atmospheric condition where air pollutants are present in concentrations that are a concern, or even an immediate danger, for human health, ecosystems or infrastructure. Exposure refers to the condition when air pollutants reach individuals (e.g. through breathing), while dose is the actual amount taken up by the human body (e.g. mass of a pollutant that reaches the blood vessels of an individual in a given time).

The harm of air pollutants can be immediate and catastrophic. In 1984 a storage tank located on the outskirts of the city of Bhopal, India, ruptured due to an accident when water was entering through leaking valves. The unintentional exothermic reaction caused methyl isocyanate to vapourize and form a highly toxic cloud. Remaining close to the ground, the contaminated plume advected into adjacent shantytowns, poisoning inhabitants. The leak caused the immediate death of ~5,000 people and more than 20,000 in the aftermath. This tragedy was the result of a series of errors. The primary one was the decision to place such a risky industrial facility in a highly populated urban area, where any accident was likely to cause great harm. That was compounded by poor maintenance of the facility and insufficient training of the staff (Varma and Varma, 2005).

Knowledge about the atmospheric dispersion of chemicals, and their potential reactions, in urban areas is essential to assess the potential threat posed by such events. For example, local-scale dispersion models (Sections 11.2.2 and 11.2.3) can help assess which area is at risk near facilities involving storage, transport and processing of dangerous goods. Further, their results help to inform the required emergency response actions.

More commonly, the harm by air pollution is due to long-term exposure to elevated concentrations that cause chronic damage. Air pollutants that originate from industrial sources and the many engines and furnaces that burn fuel across a city, contaminate the overlying atmosphere. Under unfavourable meteorological conditions air pollutants may accumulate and progressively degrade air quality in the urban boundary layer (UBL). The World Health Organization (WHO) estimates that worldwide, exposure to air pollutants results in about 7 million premature deaths per year (WHO, 2014). About 4.3 million of these are attributed to indoor air pollution in less economically developed countries (LEDC). The remainder are due to outdoor air pollution, which is primarily an environmental health problem in heavily urbanized regions of middle- and high income countries.

Urban air pollution can be managed and reduced by targeting emission processes, for example, by requiring proper technological measures, such as emission control systems, fuel switches, efficient use of resources and enforcing restrictions on the use of vehicles and other sources. Emission control tackles the problem at its origin. Management of air pollution is also achieved by improving the location and height of the point of release and promoting dispersion by proper design considerations (see Section 15.3.3). Weather conditions worsen or improve air quality for a given set of emissions. Grid models that predict airflow and air pollutant dispersion, and that incorporate atmospheric chemistry, can provide forecasts of air quality over cities and inform mitigation actions. They can also be used to project potential impacts when siting industries or infrastructure and hence minimize adverse impacts (see Section 11.3.3).

Air pollutants spread far beyond the city limits to affect distant places across a range of space and time scales. In fact, the specific nature of the emissions from a city produce a plume with a unique mixture of chemical constituents. For example, if this includes sulphur dioxide (SO₂) and nitrogen dioxide (NO₂), given sufficient time they will be transformed into sulphuric and nitric acids, respectively. When they are deposited they damage terrestrial and aquatic ecosystems (acid deposition). Similarly, the emission of greenhouse gases (GHGs) from cities change the composition of Earth’s atmosphere and alter its radiative
Table 11.1 Selected major chemicals that are medium to long-lived air pollutants emitted in cities (in alphabetical order), their source, health and environmental effects and scales of impact whether they have are a major contributor (•) to air pollution problems at the given scale or a minor contributor (○).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Major emission sources in urban areas</th>
<th>Impact on human health</th>
<th>Impact on environment and infrastructure</th>
<th>Scales of major concern</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide (CO₂)</td>
<td>The major product emitted during all fuel combustion. Also released by respiration of humans, animals, vegetation and soils.</td>
<td>Even high concentrations not toxic, but high density can accumulate in basements and poorly ventilated rooms and reduce / displace oxygen.</td>
<td>Most important long-lived greenhouse gas – alters global radiative forcing and therefore driver of anthropogenic climate change.</td>
<td>○</td>
</tr>
<tr>
<td>Carbon monoxide (CO)</td>
<td>A primary pollutant from oxygen-limited (incomplete) combustion in motor vehicles, industrial processes and domestic heating.</td>
<td>Interferes with absorption of oxygen by haemoglobin resulting in oxygen deprivation. Low-to-moderate dosages cause headaches, impair brain functions and reduce manual dexterity. At high concentrations death ensues. Heavier than air.</td>
<td>Affects animals the same way as humans. Contributes to formation of the greenhouse gases CO₂ and O₃ when oxidized.</td>
<td>• □ ○</td>
</tr>
<tr>
<td>Halocarbons and halogenated gases</td>
<td>A class of inert gases including CFC-11, CFC-12 and SF₆. Used as insulating gases, fillings or refrigerants in consumer goods, in the electrical, polymer and metal industry.</td>
<td></td>
<td>Halocarbons and halogenated gases contribute to O₃ depletion in the stratosphere. Many are very long-lived (and hence effective) greenhouse gases.</td>
<td>•</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>A toxic metal used as petroleum additive in certain countries and released during combustion. Also industrial sources.</td>
<td>Affects nervous system, kidneys, liver and blood-forming organs. Increases blood pressure and disturbs kidney and reproductive functions. Can cause brain damage, impaired mental development and reduced growth.</td>
<td>Persistent when deposited on terrestrial or aquatic ecosystems. Affects ecosystem functioning, animal reproductivity and accumulates in food-chains.</td>
<td>• □ ○</td>
</tr>
<tr>
<td>Methane (CH₄)</td>
<td>By-product of fuel combustion, and fugitive emissions from leaking of natural gas pipes and pipelines. Anaerobic decomposition (e.g. sewage, landfills)</td>
<td></td>
<td>Second most important long-lived greenhouse gas.</td>
<td>•</td>
</tr>
<tr>
<td>Nitrogen oxides (NO, NO₂)</td>
<td>Primary and secondary pollutant resulting from fuel combustion in motor vehicles, coal-, oil-, and gas-fired power stations, industrial boilers and waste incinerators. Minor emissions occur naturally from soils.</td>
<td>Acute exposure causes respiratory diseases (coughs, sore throats) and at high concentration inflames airways and reduces lung functioning. Can aggravate bronchitis, asthma and emphysema.</td>
<td>Contributes to the eutrophication of aquatic ecosystems.</td>
<td></td>
</tr>
<tr>
<td>--------------------------</td>
<td>-------------------------------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------------------------------</td>
<td>--------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Nitrous oxide (N₂O)</td>
<td>Minor combustion by-product of fuel combustion, emitted from soils, primarily managed (fertilized) greenspace.</td>
<td></td>
<td>Important long-lived greenhouse gas.</td>
<td></td>
</tr>
<tr>
<td>Non-methane volatile organic compounds (VOC)</td>
<td>Gasoline vehicle exhausts, leakage at fuelling stations, paint, manufacturing, solvents. Biogenic emissions from trees.</td>
<td>Some compounds are carcinogenic. Selected VOCs cause eye and mucous membrane irritation, others may cause fatigue and difficulty concentrating.</td>
<td>Selected compounds damage vegetation.</td>
<td></td>
</tr>
<tr>
<td>Ozone (O₃)</td>
<td>Secondary pollutant formed in urban areas primarily from VOCs and NOₓ, but also CH₄ and CO can play a role in O₃ formation at larger scales.</td>
<td>Damages respiratory tract and impairs lung function. Physical activity increases the dosage. Long-term exposure may result in decreased lung capacity and premature mortality.</td>
<td>Higher concentration can damage vegetation leading to reduced plant growth. O₃ is a short-lived greenhouse gas changing radiative transfer in the troposphere.</td>
<td></td>
</tr>
<tr>
<td>Particulate matter (PM10, PM2.5, UFP)</td>
<td>Emitted as primary pollutant during combustion (low-temperature fires, diesel vehicles, waste incinerators, domestic heating and cooking), released during mechanical abrasion (road dust, construction) or formed as secondary pollutant from SOₓ, NH₃ and NOₓ.</td>
<td>Can reach sensitive parts of the respiratory system. Exposure to fine particulates reduces lung function, increases cardiovascular and respiratory diseases and may cause premature mortality.</td>
<td>Changes radiative transmission in atmosphere (Chapter 5), can impact cloud droplet size distribution (Chapter 10) and alter radiative forcing on global scale. When deposited on snow and ice surfaces, changes their albedo.</td>
<td></td>
</tr>
<tr>
<td>Polycyclic aromatic hydrocarbons (PAH)</td>
<td>Benzene (C₆H₆) and Benzo(a)pyrene (BaP) are the most relevant PAHs and are emitted during incomplete combustion in vehicles, domestic heating, organic material (wood) and oil refining.</td>
<td>PAHs irritate the eyes, nose, throat, and bronchial tubes (BaP). Benzene and BaP are carcinogenic for humans, and harm immune system and central nervous system, blood production. Can cause leukaemia and birth defects.</td>
<td>Many PAHs have acute toxic effects on aquatic life and birds and damage leaves of plants. Selected PAHs bio-accumulate in food-chains.</td>
<td></td>
</tr>
<tr>
<td>Sulphur dioxide (SO₂)</td>
<td>Primary pollutant emitted during combustion of sulphur-containing fuels (coal, diesel, fuel oil), and in industrial processing.</td>
<td>Exacerbates asthma causing wheezing, shortness of breath and coughing and inflammation of respiratory tract. Synergistic effects with exposure to O₃ and particulate matter.</td>
<td>Damages buildings. Causes acidification of soils and aquatic ecosystems downwind of emissions, can damage forests ecosystems. Contributes to the formation of particulate matter.</td>
<td></td>
</tr>
</tbody>
</table>
budget, especially that of the troposphere (Chapter 13).

Proper understanding and management of air pollution at all scales requires complete understanding of the ‘life cycle’ of air pollutants at the scale of interest. This includes knowledge of (1) their emission or formation, (2) their dispersion and transport, and (3) their transformation and eventual removal from the atmosphere (Figure 11.2). Sections 11.1.1 to 11.1.3 provide an overview of the relevant processes involved.

11.1.1 Emissions

Air pollutants originate from anthropogenic and natural sources, although in most cases the anthropogenic sources dominate in an urban environment. Primary pollutants are those directly emitted into the atmosphere and retain their chemical character. They arise from chemical processes during fuel combustion, or releases such as leakage from pressurized storage or pipes (fugitive emissions), suspension or evaporation into the atmosphere. Biological processes also generate emissions that can be relevant in urban air pollution chemistry.

Pollutants formed in the atmosphere from primary pollutants are called secondary pollutants. Probably the best known secondary pollutant is ozone (O₃), formed from a suite of reactions of primary pollutants that become chemically transformed in the urban plume. The transformations take time, because they require a specific mix of primary pollutant concentrations and incoming solar radiation (Section 5.3.2). Disentangling the pathway from primary sources to secondary pollutant formation is a challenge that requires numerical models that incorporate the appropriate meteorological and chemical processes in the urban atmosphere.

Combustion

The majority of indoor and outdoor air pollutants are emitted during combustion. Combustion is the sum of chemical reactions between hydrocarbons and atmospheric oxygen (O₂) that produce heat and light, and release carbon dioxide (CO₂) and water vapour into the atmosphere. The dominant hydrocarbons involved are fossil fuels (e.g. natural gas, gasoline, diesel and coal) and biofuels (e.g. wood, bioethanol and biodiesel). If there is an inadequate supply of O₂, the combustion process is incomplete and part of the carbon is released as the toxic gas carbon monoxide (CO), instead of CO₂. Often furnaces and power plants are equipped with oxygen sensors in the exhaust stack to ensure an adequate supply of O₂ to
reduce incomplete combustion and CO. If combustion occurs in a very high temperature environment (typical of internal combustion engines), atmospheric nitrogen (N₂) reacts with O₂ to form nitrogen dioxide (NO₂) and nitric oxide (NO). Further, impurities of non-carbon and non-hydrogen elements in the fuel such as nitrogen or sulphur also inject NO, NO₂ and SO₂ as by-products into the atmosphere. Modern cars are equipped with catalytic converters to partially remove such air pollutants.

Apart from gaseous pollutants, combustion also releases aerosols (Chapters 5 and 10). In the context of air pollution, aerosols are usually referred to as particulate matter (PM). PM includes both solid and liquid particles in the atmosphere and exists across a wide range of sizes, varying in diameter from > 100 μm to <0.1 μm. Smoke, diesel exhaust, coal fly-ash, mineral dust, paint pigments all contain particulates, mostly made of carbon or silica, but also iron, manganese, chromium, copper and toxic metals such as lead, cadmium, nickel or beryllium. The impact of PM on human health depends partly on its size: PM between 15–100 μm is trapped in the nose and throat, while that in the 5–10 μm range reaches into upper parts of the lung, particles smaller than 5 μm reach into the fine airways of lungs, and the finest PM (< 2.5 μm) can become dissolved in the bloodstream. Air pollution management uses the terms PM10 for PM < 10 μm (possibly entering the lung), PM2.5 to quantify PM < 2.5 μm (possibly entering the bloodstream) and ultrafine particulate matter (UFP) is < 100 nm.

Fugitive and Evaporative Emissions

Fugitive emissions describe the unintended ‘escape’ of gases held in pressurized containers (e.g. tanks and pipes) that diffuse into the atmosphere. The dense network of natural gas pipes in many urban areas can be a significant source of fugitive hydrocarbon and methane emissions, if it is poorly maintained and leaky. Also, liquefied petroleum gas (LPG) is used as a major energy source for cooking and space heating in cities of LEDC. Leaks of unburned LPG can substantially contribute to air pollutant emissions in cities and play a major role in O₃ formation (Blake and Rowland, 1995).

Evaporative emissions occur when liquids, with a low boiling point, evaporate. In cities volatile organic compounds (VOC), which have a relatively high vapour pressure at ambient temperatures, are a significant concern because they are found in many processes and products. VOCs vapourize from solvents, paints, vehicle fuelling stations, fuel storage facilities, refineries and in various industrial processes. Evaporative emissions increase with the ambient temperature (Rubin et al., 2006).

Biogenic Emissions

All living organisms, including humans, animals and vegetation, constantly exchange gases as part of their metabolic activity. In the process of respiration, humans, plants and microbes release the non-toxic GHG CO₂. Some microbes and fungi emit toxins that lead to diminution of indoor air quality; many tree and plant species emit specific VOCs, such as isoprene and more complex terpenes that promote chemical reactions leading to the formation of O₃. Emission of terpenes by trees depends on physiological controls, air temperature and light availability and hence exhibits a marked diurnal pattern (Guenther et al., 1993) and it also depends on tree species; substantial contributors are oaks, poplars, eucalypts, pines, sycamore and thuja.

11.1.2 Dispersion and Transport

Once released, air pollutants become part of the air. Unlike temperature or pressure, they do not have a direct effect on airflow, therefore they are considered to be passive scalars transported by, but not modifying, the airflow. However, it is worth stating that many air pollutants, in particular PM and GHGs, modify radiative transfer processes that impact airflow at longer time scales.

Concentration and Mixing Ratio

The abundance of air pollutants in the atmosphere is quantified as a concentration χ, i.e. mass per volume of air (e.g. μg m⁻³). Concentrations are not conservative because they depend on the density of the air, therefore molar mixing ratios r (mole of an air pollutant per mole of air, e.g. μmol mol⁻¹) are also used: they are conserved even as an air parcel undergoes thermodynamic changes. For trace gases in the atmosphere, r is typically expressed in parts per million (ppm = μmol mol⁻¹) or parts per billion (ppb = nmol mol⁻¹). For trace gases, concentration χ (μg m⁻³) and molar mixing ratio r (in ppm) can be converted by the ideal gas law:

\[ r = \frac{\chi}{\rho_a M_p} \]  

Equation 11.1
where, $M_p$ is the molar mass of the air pollutant (in g mol$^{-1}$), $M_a$ is the molar mass of dry air (28.96 g mol$^{-1}$), and $\rho_a$ is current (dry) air density (in g m$^{-3}$).

Note that Equation 11.1 is only applicable for gaseous pollutants, for example, it does not hold for PM or liquid droplets, which can only be expressed as a concentration.

**Dilution**

As a scalar, air pollutants are advected by the mean flow and mixed by turbulence, which relocates them and dilutes their concentration. The effect of wind speed on air pollutant concentration is illustrated in Figure 11.3 where a chimney stack emits an air pollutant at the constant rate of one puff every second. If the wind speed ($\bar{u}$) is 2 m s$^{-1}$ there will be 2 m between puffs; but if $\bar{u}$ is 6 m s$^{-1}$ they will be spaced every 6 m. Thus the higher the wind speed, the greater is the volume of air passing the stack per unit time, and the smaller the concentration downwind of the stack exit.

**Turbulent Mixing**

Greater speeds also mean greater turbulence that disperses air pollutants. The effect of turbulence depends on the difference between the scale of the pollution (the puff) and the typical eddy size (Figure 11.4). Eddies created by mechanical effects have characteristic sizes that match the dominant roughness elements in a city (buildings, trees). Eddies created by thermal effects have a characteristic size that is set by surface temperature differences. The upper limit for eddies is the mixed layer (ML) depth $z_I$.

If the characteristic eddy size is much smaller than the puff, the effect of turbulence causes the puff to grow relatively evenly in the vertical and horizontal directions (Figure 11.4a). For a continuous source, such as the exhaust from a stack, this results in a cone-shaped plume that grows both laterally and vertically downwind of the point of release. This situation is typical of emissions from high stacks over relatively smooth and uniform terrain in the absence of thermal effects. If the typical size of the eddy is close to that of the puff, it becomes stretched and distorted (Figure 11.4b). This is a feature of emissions occurring closer to the urban surface, for example. Finally, if the characteristic eddy sizes are much larger than the puff dimensions, then the entire puff may be simply advected by turbulence without much distortion (Figure 11.4c).

Knowledge of the scale of turbulence, and the overall turbulent kinetic energy (TKE) is essential to be able to properly predict air pollutant dispersion in an urban environment. Stability further modifies this situation because the vertical spread may become quite different from the lateral spread. For example, a plume in a stable atmosphere is often said to be fanning, where lateral dispersion is much larger than in the vertical because vertical movements are suppressed. Conversely, in unstable conditions, dispersion happens preferentially in the vertical direction.
causing an effect called looping. Urban atmospheres tend towards neutrality (see Chapter 7) hence dispersion patterns typical of strong stability (fanning) or strong instability (looping) are relatively rare.

11.1.3 Removal and Transformation

Without removal, air pollutants would accumulate in the atmosphere, and concentrations would continuously increase. In fact, this happens to many GHGs that remain for decades to centuries in the atmosphere (Chapter 13). Their accumulation alters radiative transfer and modifies the climate system. Most other air pollutants are removed sooner after emission by four processes: gravitational settling; dry deposition; wet deposition and; chemical reactions and/or decay.

Gravitational Settling

Gravitational settling is responsible for the removal of heavier particulates from the atmosphere. The terminal settling velocity \( v_s \) (in m s\(^{-1}\)) of particles determines the rate of removal, as particle mass increases, higher terminal settling velocities will be reached. Most PM > 10 \( \mu \)m in diameter settles out relatively rapidly, in closer proximity to emission sources and even strong turbulence is unable to hold these particles in suspension for long. The descent of smaller particles is slowed by turbulence, and those < 1 \( \mu \)m in diameter remain aloft for weeks to months (see Figure 5.3). Gaseous pollutants can be adsorbed onto particles that settle gravitationally and be removed with them.

Dry Deposition

Dry deposition is a transfer process similar to that involved in the vertical transfer of heat, water vapour and momentum to and from surfaces. In this process gases and particles are transported by turbulent mixing to surfaces (ground, walls, roofs, vegetation), however to actually reach the surface, they need to cross the thin laminar boundary layer (LBL) attached to all surfaces, this is achieved by means of diffusion. This can be expressed as a vertical mass flux density \( F_p \) of an air pollutant (in \( \mu \)g m\(^{-2}\) s\(^{-1}\)) where the underlying surface acts as a pollutant sink. In analogy with the turbulent transfer of heat and water (Section 6.4), the vertical transfer of the air pollutant through the turbulent boundary layer can be described by a covariance of vertical wind and concentration:

\[
F_p = \frac{\overline{w'p'}}{\Delta z} \quad (\mu g m^{-2} s^{-1}) \quad \text{Equation 11.2}
\]

The vertical flux of an air pollutant \( F_p \) in the LBL is due to diffusion:

\[
F_p = -k_p \frac{\partial C}{\partial z} \quad (\mu g m^{-2} s^{-1}) \quad \text{Equation 11.3}
\]

where the flux is proportional to the molecular diffusivity \( k_p \) (in m\(^2\) s\(^{-1}\)) and the vertical gradient in the mean pollutant concentration in the LBL. The flux through both the turbulent and LBLs can be expressed as a deposition velocity \( v_d \):

\[
F_p = v_d \Delta C \quad (m s^{-1}) \quad \text{Equation 11.4}
\]

The deposition velocity \( v_d \) is a conductance. Its reciprocal can be written as the sum of various resistances (Section 6.4), including the aerodynamic resistance \( r_a \) for the turbulent layer, the LBL resistance \( r_L \), and for gases the surface resistance \( r_s \) which accounts for the ability of the surface to absorb the gas:

\[
v_d = \frac{1}{r_a + r_L + r_s} \quad (m s^{-1}) \quad \text{Equation 11.5}
\]

For a given atmospheric mean concentration, the rate at which an air pollutant is delivered to the surface is governed by the value of the deposition velocity, which in turn depends upon the state of turbulence and molecular / surface properties. The surface resistance \( r_s \) varies with the type of surface. For example, on a leaf surface the stomatal aperture partly controls \( r_s \), while over soil it is affected by bacterial activity, and over water by the surface tension. It may also be affected by electrostatic attraction, and chemical reactions between the surface materials and the pollutant.

Wet Deposition

Some of the PM, especially if hygroscopic, becomes cloud condensation nuclei (CCN, see Section 10.1) around which water or ice condenses to form a droplet or ice crystal in clouds. Further, particulates and gases can then collide with existing droplets and ice crystals. This is most efficient for small particles (< 0.1 \( \mu \)m) and gas molecules. Molecules and particulates that collide with a droplet are then dissolved up to the limit given by the solubility of the pollutant in water. For example, the solubility of gaseous pollutants such as SO\(_2\) and NO\(_2\) is higher than it is for O\(_3\). This in-cloud pollutant scavenging process is called rainout (or snowout).

Eventually, if the droplet becomes large enough, it is precipitated and transports the pollutants with it to the surface. Below cloud level, precipitation also
cleanses the air by ‘sweeping-out’ some PM. As drop-
lets or ice crystals fall they can collide with particles
and carry them to the surface (washout). This process
is most efficient for larger PM (> 1 μm). Altogether, a
precipitation event removes pollutants in the form of
CCN, dissolved gases and particles involved in colli-
sions and entrained during the descent. A rainstorm
can transform a murky haze into visibly cleaner envir-
onment. Note that PM between ~0.1 and 1 μm are not
efficiently removed by gravitational settling, rainout
or by washout. This explains why particles in this size
range remain longer in the atmosphere than larger or
smaller ones. Note also that whereas many pollutants
are efficiently removed from the atmosphere by wet
deposition, they are still deposited on the ground
where they can pollute aquatic and terrestrial ecosys-
tems (‘acid deposition’, see Section 11.4.2).

Chemical Reactions and Decay

The mechanisms discussed so far remove air pollutants
by mechanical and microphysical means, but chemical
reactions are also crucial in air pollution climatology.
While some reactions may aid in the decomposition and
decay of air pollutants, others lead to the formation of
new secondary pollutants. Some reactions happen di-
rectly in the gas-phase by collision of molecules, while
others are more efficient if the air pollutant is dissolved
in a liquid droplet or is adsorbed on a particle. Chemical
reactions in the atmosphere are generally classified as
thermal or photochemical. Thermal reactions involve
the collision of two gas molecules. A very common class
of thermal reactions transform gases into more oxidized
states, such as atomic oxygen (O), the hydroxyl
radical (OH) or the hydroperoxyl radical (HO2),
which immediately react with other molecules.

11.1.4 Scales of Air Pollution

Air quality is relevant at many scales of inquiry. Table 11.1 lists common air pollutants, their sources,
impacts on human health and the environment gener-
ally and identifies the scales at which the problem is
greatest. The scale of the pollution is largely dictated
by the atmospheric residence time (i.e. the average
time before removal) and its effects on health and
ecosystems.

Figure 11.5 links the residence time of common air
pollutants to their characteristic horizontal distance of
dispersion. Short-lived radicals such as OH or HO2
have residence times of seconds to minutes, so their
dispersion in the atmosphere is very limited (lower left
of Figure 11.5). At micro- and local scales, air pollu-
tion is characterized by primary pollutants from combus-
tion, with considerable small-scale variability due to
the specific arrangement of emission sources interact-
ing with the complex wind field and/or indoor venting patterns surrounding buildings, urban blocks
and neighbourhoods, characteristic for the UCL. Thus
air pollutants from one street can be channelled at
intersections into adjoining streets, or be trapped in
a recirculating eddy at an intersection. Some eventu-
ally settle or are captured inside the UCL on building
or road surfaces and vegetation and some are swept
from the UCL by turbulence into the overlying UBL.

In the UBL, typical air pollutants emitted from
individual sources (cars, buildings, industry, etc.) mix
and transform over time to form a characteristic
urban blend, commonly containing CO, NO2, SO2
and/or O3. Without a regional wind, urban breezes
create a polluted urban dome (Figure 2.12a). With a
regional wind, the contaminated UBL extends down-
wind as an urban plume (Figure 2.12b).

At the regional to global scale, long-lived species
such as GHGs have residence times of years to cen-
turies (upper right of Figure 11.5). The individual
contributions of cities across the globe become well-
mixed in their corresponding hemisphere and add to
those from other sources. Since emissions exceed rates
of removal, this can steadily increase global back-
ground concentrations of certain gases. They are
effectively changing radiative forcing for the planet; a
major cause of anthropogenic climate change
(Chapter 13).

The rest of this chapter is organized according to
scale. Section 11.2 focuses on pollution at small
scapes – buildings, single sources and the UCL.
Section 11.3 deals with the pollution of the UBL and the processes that cause persistent outdoor air quality problems in cities. Section 11.4 discusses regional to continental impacts of urban pollutant emissions.

In this chapter we restrict discussion to simple, generic circumstances, even though most cities are located in more complex terrain (orography, shorelines). In those places air pollution is the outcome of interplay between characteristic emissions, local wind systems, topography and the background climate. This creates unique challenges to the management of air pollution. These issues are discussed in Chapter 12.

### 11.2 Micro- and Local-Scale Air Pollution in Cities

The urban canopy layer (UCL) is the zone of human occupation and the quality of the air in it is critical in any assessment of the public health consequences. A great many emission sources are located within the UCL where contaminants are injected directly into the indoor or outdoor air, close to breathing level. Here air pollutants encounter a great variety of microscale conditions that inhibit or enhance their dilution. Our goal is to predict their dispersion and venting out of the UCL, where they eventually mix with emissions from sources at or near roof level. At the local scale, the aggregate effect of microscale processes within the roughness sublayer (RSL) is to mix all emissions together so they can be considered to arise from a neighbourhood. To this must be added other sources of pollution, such as those from chimney stacks that are emitted directly into the atmosphere above mean roof height. The overall outcome is an urban ISL that is contaminated to a greater or lesser degree with great variability in time and space. From an air quality management perspective, the challenges are to: (i) identify the ambient conditions to which the population is exposed over the course of a day, month, year, or lifetime; (ii) to assess the health consequences and; (iii) to regulate emissions so as to limit exposure. At the outset, it is worth distinguishing between the
indoor and outdoor environments, which reflect very
different ambient conditions.

11.2.1 Indoor Air Pollution
For a great deal of urban living, an indoor environ-
ment represents ambient conditions. In fact, indoor
air pollution could be of greater concern than that
outdoors, simply because most dwellers spend sub-
stantially more time inside buildings and vehicles
and in many activities (domestic and occupational)
the emission of air pollutants first occurs within a
confined indoor setting. However, the health conse-
quences of exposure to many of the air pollutants
found indoors have not been examined to the same
extent as the common outdoor air pollutants.

As a simplified, yet illustrative, model of indoor
pollution, the rate of change of pollutant concen-
tration for a given indoor air volume $V$ (in m$^3$) can be
described:

$$ \frac{\partial \chi_i}{\partial t} = \frac{E}{C_0} - D \chi_i + X \frac{\chi_a}{C_0} \chi_i \left( \frac{V}{\mu g m^{-3} s^{-1}} \right) $$

Equation 11.6

This is a simple ‘box’ model as illustrated in
Figure 11.6, where $\chi_i$ is the time-averaged indoor air
pollutant concentration, and $\chi_a$ is the air pollutant
concentration of the outdoor air (both in $\mu g m^{-3}$). $E$
is the sum of all indoor emissions of the air pollutant
of interest (in $\mu g s^{-1}$). The major sources of indoor air
pollutants are fuel combustion, smoking and cooking,
and fugitive and evaporative emissions from furniture,
walls and ground in the living space. The venting rate
$X$ (in m$^3$ s$^{-1}$) describes the rate of air volume
exchanged between indoors and outdoors through
windows, doors, chimneys, cracks and by forced ven-
tilation. $X$ depends on the construction details and the
outdoor air flow (pressure differences across building).

Indoor air pollution is of biggest concern in cities of
LEDCs, especially where solid fuel combustion (for
cooking and heating) occurs within spaces that are
crowded and poorly ventilated. However, unhealthy
indoor air is not restricted to poor quality housing and
low-quality fuel use. It can also be a feature of some
modern buildings designed to be energy efficient, these
buildings are nearly completely sealed so that indoor-
outdoor exchanges are tightly controlled and much of
the indoor air is recirculated. In such circumstances,
even small pollutant emission rates can result in high
concentrations over time.

The list of pollutants found in indoor air is huge —
the following sections are an attempt to classify some

Figure 11.6 Mass balance of an indoor air volume.
of the most common air pollutants by their emission process – combustion, evaporation and suspension, leakage and biological processes.

**Combustion By-Products**

Many indoor air pollutants are, similar to outdoor air pollutants, released during combustion for space heating, hot water generation, cooking and/or smoking. The major air pollutants of concern are the primary pollutants CO, NOx, PM and carcinogenic organic by-products, such as polycyclic aromatic hydrocarbons (PAH, see Table 11.1). To a lesser extent, selected secondary pollutants such as O₃ can also be of concern indoors.

Combustion of solid fuels (wood, dung, agricultural residues, coal) often takes place in simple stoves or open fires indoors with an inadequate supply of oxygen, this causes incomplete primary combustion by-products such as CO, PM and VOCs. Exposure to those air pollutants can lead to chronic and acute health risks. Globally, indoor pollution from solid fuel combustion is on the list of the top 10 health risks that cause overall mortality, and it is the single most important environmental health risk (WHO, 2009).

Estimates from dwellings in India suggest indoor exposure to PM is much greater than that experienced outdoors. Table 11.2 shows the ambient levels of PM10 when averaged over 24 hours in ‘typical’ exposure environments for different income levels in Delhi, India. While all income levels experience approximately similar outdoor air quality, they are distinguished by their different exposure in domestic or occupational settings, and access to affordable fuels. The lowest income class are more likely to cook over open solid fuel fires and occupy small, poorly ventilated dwellings. Moreover, as cooking is traditionally a female role, the dosage received by females is higher than that of males in the same income group.

For CO, high concentrations are reported inside cars and buses where they are usually 2–5 times those measured in adjacent streets. Inhalation of high concentrations of CO in buildings emitted from gas stoves, vehicles in garages and other combustion engines are the most common means of poisoning – these also occur in cities of more economically developed countries (MEDC). Occasionally deaths from CO poisoning are reported, usually due to improper venting of appliances and because victims are often rendered unconscious in their sleep.

There are well-established dose-response relationship between tobacco smoke and chronic respiratory symptoms — not only for smokers but also for individuals simply exposed to environmental tobacco smoke (i.e. ‘passive smoking’). For example, it has been shown that exposure of children to passive smoking in indoor settings increases their risk of developing asthma between 40% and 200% (e.g. Cook et al., 1998). From a public health perspective, passive smoking is the most relevant indoor pollution source in most middle- and high income countries.

**Evaporation and Suspension**

In contrast to the chemical process of combustion, a host of other air pollutants are released constantly by the built environment through physical processes, including (i) evaporation of volatile compounds, (ii) suspension of fine particulates, and (iii) diffusion from pressurized natural gas pipes.

Evaporative emissions of VOCs indoors can originate from furniture, consumer products and

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**Table 11.2** Exposure to PM10 concentration and time spent in different microenvironment settings as a function of income class in urban India, for the city of Delhi (Modified after: Kandlikar and Ramachandran, 2000).

<table>
<thead>
<tr>
<th>Microenvironment</th>
<th>Low income</th>
<th>Medium income</th>
<th>High income</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooking</td>
<td>1,000–4,000 μg m⁻³</td>
<td>350–600 μg m⁻³</td>
<td>200–300 μg m⁻³</td>
</tr>
<tr>
<td></td>
<td>1–2 h</td>
<td>2–3 h</td>
<td>1–2 h</td>
</tr>
<tr>
<td>Non-cooking</td>
<td>650–800 μg m⁻³</td>
<td>200–300 μg m⁻³</td>
<td>200–300 μg m⁻³</td>
</tr>
<tr>
<td></td>
<td>10–12 h</td>
<td>12–14 h</td>
<td>12–14 h</td>
</tr>
<tr>
<td>Occupational</td>
<td>650–800 μg m⁻³</td>
<td>200–300 μg m⁻³</td>
<td>200–300 μg m⁻³</td>
</tr>
<tr>
<td></td>
<td>12–14 h</td>
<td>8 h</td>
<td>8 h</td>
</tr>
<tr>
<td>Outdoor</td>
<td>200–700 μg m⁻³</td>
<td>200–700 μg m⁻³</td>
<td>200–700 μg m⁻³</td>
</tr>
<tr>
<td></td>
<td>1–2 h</td>
<td>1–2 h</td>
<td>1–2 h</td>
</tr>
</tbody>
</table>
construction materials. A prominent example is formaldehyde released from particle board, insulation and furnishings. Many other organic compounds evaporate from adhesives, solvents and paints (e.g., toluene, styrene, alcohols, acetaldehydes and terpenes). In typical indoor air, a few hundred different VOCs are traceable, and their chemical ‘mix’ is sometimes sensed as the characteristic odour of buildings. The sum of all VOCs is expressed as the concentration of total volatile organic compounds. At the time of initial occupancy, typical office buildings have been shown to contain indoor air with 50 to 100 times higher total VOC concentrations than outdoor air (Bluyssen et al., 1996). Unsurprisingly, it is challenging to isolate health impacts of individual indoor VOCs given the complexity of the total chemical mix – however, effects attributed to selected VOCs in health studies include mucous membrane and eye irritation, fatigue and carcinogenicity.

The most hazardous indoor air pollutant is asbestos, a class of long and flexible or crystalline mineral fibres. Asbestos fibres are released from the wearing down of selected manufactured products and construction materials (pipes, fire retardants, floors, tiles, insulation). Being particulates, asbestos fibres can remain suspended in the indoor and outdoor air for long periods and are transported by airflow through air conditioning systems. As for PM, heavier particles settle more quickly. The major concern is that asbestos fibres are very persistent — they cannot evaporate or dissolve in water and if they reach human lungs, they accumulate and damage the tissue.

Radon Venting

A unique case of indoor air pollution is caused by radon, an inert radioactive gas. The isotope radon-222 is naturally formed in rocks and soils by radioactive decay of certain minerals containing uranium (e.g. pitchblende). It decays with a half-life of 3.8 days to more stable products that are also radioactive, but not gaseous (lead, bismuth, polonium deposited on particles). Because radon is an inert gas, it can escape easily through cracks and fissures into tunnels, pipes and basements of buildings. Radon-222 accumulates indoors due to low ventilation rates. When inhaled, it deposits its non-gaseous and radioactive daughter products on the lung tissues where they remain, irritate cells and can cause cancer. After tobacco smoke, radon inhalation in indoor settings is the second most important cause of lung cancer worldwide, and is responsible for 3 to 14% of all mortalities (WHO, 2009). Radon isotopes also account for roughly half of the general population’s exposure to ionizing radiation. There are large regional differences, due to varying near-surface geology and differences in building construction practice.

The micro- and urban meteorological aspect of radon pollution concerns its transport from the soil to the indoor space and eventually to the outdoor atmosphere (Nazaroff, 1992). Typical concentrations of radon-222 in soil pores result in radioactivity of several 10,000 Bq m\(^{-3}\) in the ground. The escape of radon to the overlying atmosphere depends on soil porosity and the pressure gradients in the soil. Although the airspace in soil pores is in constant exchange with the outdoor air, in most cases the soil airspace is renewed very slowly because of the less permeable organic top-soil and the presence of sealed surfaces (asphalt, concrete) in urban areas that form a ‘lid’ over the bedrock. If radon reaches the outdoor atmosphere, it is quickly dispersed and diluted. The radioactivity in the outdoor space near the ground is small compared with that of soil (2–10 Bq m\(^{-3}\)). Nevertheless, radon-222 in buildings is a problem; and on average it reaches radioactive levels between 20–400 Bq m\(^{-3}\), but in unfavourable cases can exceed 10,000 Bq m\(^{-3}\), which is highly unhealthy. Buildings with poorly sealed basements are a particular concern. Firstly and obviously, the small volume and restricted venting of buildings prevents effective dispersion compared to the outdoor atmosphere. Secondly, in buildings with basements, the top-soil has been removed hence the less permeable lid is missing, in particular if the basement has a natural floor. Also a generally lower soil moisture underneath buildings means higher permeability for gases in the soil. Thirdly, the airflow around the building envelope causes pressure differences (see Section 4.2.1) that affect the pressure in the soil and building interior causing preferred venting of radon from underneath buildings. The negative pressure in buildings caused by active ventilation and heating can further ‘suck’ radon-222 from the subsurface through cracks in the bottom slab or walls into indoor spaces. Radioactivity in homes caused by radon has hence been shown to depend on outdoor wind speed and heating demand (Miles, 2001).

Biological Air Pollution

Biological contaminants, namely bioaerosols including fungi, mites, amoebae, bacteria and viruses are
present and transported in indoor air. Molds and microorganisms cause infections and allergic, and hypersensitivity reactions. Mycotoxins and certain VOCs released by these organisms are suggested to be compounds capable of causing such symptoms. Humans and animals are the source of bacteria, and viruses that spread through the ventilation systems of larger buildings.

CO₂, released by both, human respiration and during fuel combustion, is routinely used as a reliable indicator of biological indoor air pollution, especially for emissions originating from building occupants. Although not a health concern, concentrations of CO₂ more than ~1000 ppm in buildings are considered an indication of poor ventilation and indoor air quality (Zhang and Smith, 2003) and is usually accompanied by feelings of stuffiness, tiredness, headache and loss of concentration and productivity. Relatively simple sensors that monitor CO₂ can be used in combination with active control systems to increase/decrease the inflow of outside fresh air into larger buildings.

Fortunately, all indoor air pollution problems (combustion, evaporation, radon and biological contaminants) can be mitigated by adequate technical, hygienic and design measures. In this respect, overcoming educational and economic barriers to implementation is key.

### 11.2.2 Outdoor Air Pollution in the Urban Canopy Layer

Compared to indoors, air pollution climatology in outdoor urban spaces between buildings is more complex for several reasons. Firstly, emission sources in an urban system are in multiple locations. For example, emissions could originate from buildings, mobile vehicles near ground level and even from sources above roof level (e.g. chimneys) that might be drawn down into the UCL, in addition there could be biological contributions by plants and trees. Secondly, airflow itself follows complex patterns, so dispersion in the UCL must be treated as fully 3-D (Section 4.2). Thirdly, the movement of people (i.e. the ‘receptors’) through a street system exposes them to an extraordinary variety of transitory ambient conditions.

Figure 11.7 illustrates the exposure of a pedestrian to ultrafine particulates over a period of 30 min when walking through the UCL in central London, United Kingdom. Exceptionally high exposure occurs at intersections, traffic crosswalks and when passing people smoking. On their daily commute to and from work people tend to follow preferred routes of this kind. Knowledge of repeated exposure to air pollutants along such routes can be of value in evaluating exposure, threats to health and how to manage air quality at this scale.

**Figure 11.7** A pedestrian’s exposure while walking through a complex urban concentration field of ultrafine particulate matter in London, United Kingdom (Data source: A. Robins).
In many cities, air pollutant concentrations in the UCL are dominated by emissions from traffic. The primary pollutants created during the combustion of gasoline, diesel and biofuels (CO, NOx, PM, PAHs, VOCs, and in some cases lead from leaded gasoline) arise near street level but their fate very much depends on airflow patterns in the UCL. Buildings and trees produce considerable mechanical turbulence that enhances mixing and dilutes concentrations. Canyon airflow includes channelling and recirculation vortices including possible thermal effects due to patterns of sunlight and shadow created in the UCL. Given these circumstances, measuring and modelling air quality to which the urban population is exposed in the UCL is a difficult task, however, without such assessments it is not possible to manage emissions to ensure a public health. Observations of air quality must be of sufficient density to ensure the spatial and temporal variability of air pollutant concentrations in the UCL is resolved. Hence, observations must consider problematic hot-spots and episodes (that may be localized or short-lived).

Monitoring Outdoor Air Quality
Air pollution monitoring is often carried out using an observation network consisting of fixed stations deployed in the UCL to capture the average and the extreme ambient concentrations. These stations can be of two types:

- **Urban background stations** that represent ‘typical’ concentrations most people experience. The stations are usually placed in courtyards, parks, or other places away from significant pollution sources (such as major roads). They capture a spatially averaged signal representative of the lower end of concentrations typifying the local scale.

- **Roadside stations** are often used to measure pollution ‘hot-spots’; those places where concentrations are expected to be highest and to which significant numbers of people are regularly exposed (e.g. when driving or walking along streets or living in buildings flanking the street). They are typically located on a pedestrian walkway along selected busy streets, close to the traffic lanes and with the sensor inlets at 1.5 to 3 m above ground. Similar stations may be placed in the vicinity of large industrial plants.

Such networks of fixed stations are often supplemented by mobile or short-period fixed observations, to either ensure the network observations are sufficient or to monitor the effects of changes in the urban environment (e.g. new traffic regulations or large-scale construction projects).

Despite these efforts, observations alone are not sufficient to assess air quality across a city. Numerical modelling at the microscale is necessary to complement an observation network and assess the representativeness of its measurement sites. Microscale models can also guide air quality management strategies at the scale of streets and urban blocks (e.g. traffic routing and building density).

**Air Pollution in Urban Canyons**
Air quality in streets has received particular attention because of the ubiquity of these exposure environments, their relatively confined setting and the intensity of activities near ground level that generate air pollutants. The effects of traffic emissions in long and relatively narrow (small aspect ratio) streets have been well studied because the limited mixing can result in poor air quality (see Section 4.2.3 and Figure 11.1).

Air pollution in a street canyon is controlled by the emission strength, the exchange of air within the UCL and its interactions with the air above roof level. Air pollutants may be transported along a canyon or laterally into intersecting streets, courtyards and adjacent buildings or mixed with the air above roof level. Where street width is narrow and the buildings on either side form an almost unbroken wall, lateral dispersion within the UCL is restricted. Such street canyons experience skimming flow (see Figure 4.9c) meaning that above-roof winds skip along without penetrating into the UCL. Instead, UCL air and its contaminants are recirculated internally by a helical vortex. Canyon aspect ratio $H/W$ and roof shape greatly affect the vertical ventilation of such canyons (see Section 4.2.3).

Figure 11.8 shows the spatial variability of the traffic-related pollutant benzene, a carcinogenic PAH emitted during combustion of gasoline (see Table 11.1). Measurements were taken at various locations in the busy 4-lane canyon ‘Rue de Rennes’ in Paris, France and reflect the average molar mixing ratios over five consecutive weekdays. The canyon has an aspect ratio of about 1 and is bounded on either side by rows of uniform 6–7 storey buildings. Two additional measurements were taken at a distance of about 300 m on either side of the canyon at urban background locations (greenspaces). The observed benzene mixing ratios are substantially higher in the
canyon than at the urban background sites. Also there is clear cross-canyon asymmetry of pollutant mixing ratios: when the dominant above-roof winds are nearly perpendicular to the canyon axis, values on the leeward wall (left) of the canyon are higher than at the same height on the windward wall (right). At the leeward wall the helical flow pattern in the canyon causes updrafts of polluted air, whereas on the windward wall cleaner air from above roof level is entrained (see also Figure 4.11a and b). Measured mixing ratios decrease with height in the canyon; higher values are measured deeper in the canyon (closer to the source of emissions) where the legal standard is exceeded. In fact, highest mixing ratios are reported on the pedestrian walkway on the leeward side, which is immediately downwind of the road lane. This location may also experience corner vortices that further trap and recirculate air pollutants.

Temporal variations of emissions and of the flow field combine to produce characteristic pollution concentration cycles inside street canyons. Figure 11.9 shows the relation between traffic, winds and NO₂ mixing ratios over two days in a street canyon in Copenhagen, Denmark. Emissions into the street are governed by the traffic density, which shows a diurnal ‘wave’ pattern associated with a daytime peak that is shifted towards evening. Superimposed on the wave crest are two peaks associated with commuter traffic.

The NO₂ concentration in the street reflects the emissions pattern but is moderated by wind. The stronger winds on the second day have the effect of ventilating much of the contaminated air from the street, reducing mixing ratios. Note that in both cases there is a vertical gradient in NO₂ with maximum values near the source, at street level.

The pattern of pollution dispersion within such ideal street canyons is well-established and it has allowed the development of simple microscale air...
pollution models to predict concentrations inside canyons in response to street dimensions, above-roof wind direction and the rate of emissions. For example, early street canyon pollution models such as that of Johnson et al. (1973) use simple box approaches and empirical relations based on measurements to predict concentrations for receptors on the leeward and windward sides of a street canyon. Concentrations are directly proportional to the number of vehicles, and inversely proportional to the ambient wind speed and are scaled by the dimensions of the canyon. Their model adjusts wind speed for traffic effects and accounts for traffic-produced turbulence (see Chapter 4).

More sophisticated models combine box-models with plume dispersion models. As an early example, Yamartino and Wiegand (1986) developed a plume dispersion model that decomposes the above-canyon flow into two segments: a cross-canyon component (which drives a vortex) and an along-canyon component. Each flow component regulates distinct dispersion patterns of vehicle emissions that results in canyon zones where advective or turbulent processes dominate. Along the windward wall a narrow channel of fresh air from above the canyon is drawn into the street. As it descends it mixes with a proportion of recirculating canyon air, in the lower half of the street, the mixed flow crosses the vehicle-generated pollutant plume to the lee side of the street and then upwards. At the canyon top a portion of the contaminated air is advected into the above-canyon flow, while another portion diffuses and recirculates.

Today, a large number of operational street canyon air pollution models are available for use in regulatory applications (Vardoulakis et al., 2003). They can all produce time series of air pollutant concentrations within canyons based on a limited number of simple inputs (traffic volume, fleet composition, canyon geometry, meteorological data).

Air Pollution and Dispersion in Complex Geometries
In many other cases, the outdoor airspace in the UCL cannot be adequately described using simple 2-D canyon dispersion models. In such cases, more sophisticated simulations are possible using computational fluid dynamics (CFD) simulations of the flow field inside canyons (Li et al., 2006) or neighbourhoods with real buildings resolved (Tseng et al., 2006; Gio- metto et al., 2016). Those approaches are flexible, and solve Reynolds Averaged Navier-Stokes Equations (Chapter 3) or use Large Eddy Simulations (LES) to incorporate the effect of the urban structure on the flow. CFD models can track air pollutant concentrations at each grid node as passive scalars or coupled with chemical reactions. CFD approaches have high computational needs and their use to date is mostly restricted to research, and to selected subsets of cities, rather than for general regulatory purposes in air pollution management.

The population density of cities comes with increased vulnerability to accidental and intentional airborne release of hazardous gases and materials such as those in industrial and transportation accidents or by acts of warfare or terrorism. In such cases, knowledge about the dispersion, potential reactions and transformation of chemicals, and settling or deposition is required to identify areas of greatest impact, for example, to prioritize areas for evacuation or other emergency measures.

Over open and flat terrain, knowledge of wind direction and speed is usually sufficient to make a rough estimate of zones of danger after an accidental release. Observations on site, with emergency weather stations or using operational weather data, might be appropriate to estimate probable spread. Not so in urban areas, where complex flow in the UCL renders point measurements of wind nearly useless and weather forecast models are too coarse to resolve local flow features. Figure 11.10 depicts the above-ground plume released during a tragic subway fire in the city of Daegu, South Korea. Although the plume is easily identifiable and coherent, it experiences complex behaviour, changing its direction as it is first channeled along one street canyon and then helically turns by 270º as it rises above the intersection and mixes with the ambient flow. The case also illustrates the interconnectivity between different air spaces in cities, including underground space (tunnels), indoor space and the outdoor air: all are affected but to different degrees.

Figure 11.11 illustrates modelled zones of danger from a hypothetical release at ground level in Portland, United States (a) with and (b) without the effect of buildings near the release point considered. The regular arrangement of streets and buildings in (a) causes preferential channelling, which redirects the
plume centreline considerably. The presence of tall buildings greatly enhances both the lateral and vertical mixing of the hazardous material. The plume shape close to the source is completely different in the two cases, as are the predicted zones of danger. Even far downwind, on the East side of the Willamette River, the plume is broadened and shifted northwards due to diversion along the street grid.

The two examples in Figure 11.10 and Figure 11.11 illustrate that considering complexities of airflow in the UCL are crucial for successful emergency response modelling, if both the source and receptors are in the canopy. However, this requirement comes with substantial costs. Resolving buildings in modern CFD-based models is (i) computationally expensive, (ii) requires knowledge of the actual urban morphometry to be incorporated into the model and (iii) requires specialized infrastructure and personnel to run such complex models. Emergencies, on the other hand require fast action, and can happen at unpredictable places where geographical data concerning building details and topography and the necessary computational personnel might not be available.

For emergency response, predictions of the flow field and the plume spread in a building-resolving mode are needed very quickly. With current computing power this is unfortunately not yet feasible. And for most cases, the uncertainties about location, quantity, timing and the material released into an urban environment might be much larger than any fluid dynamical errors in models. Nevertheless, for selected subsets of cities and industrial infrastructure, simplified models are run operationally to assist emergency response actions. Such models may use operational
wind measurements from weather stations to determine the boundary conditions or they are informed by coarser-scale weather forecast models. That way they can predict the flow field a few hours into the future, then in case of an emergency the user can insert a suitable source and quickly determine its spread in the pre-calculated wind field. To overcome the computational load (and time required) to model the details of the flow around buildings, some schemes use coarse resolution models or run a suite of simulations under different meteorological conditions in advance and later use databases to interpolate from the pre-simulated cases (Brown, 2004).

Another application of urban-scale dispersion models is to allow authorities to be better prepared in the event of an accidental or intentional release of harmful substances. For this purpose, urban dispersion models can be run in a ‘backward mode’ to determine areas where a potential release of chemical, biological and radioactive material might affect people, ecosystems or critical infrastructure. In doing this the plume spread is inverted in time (but airflow is not) and so a model can predict risk zones, i.e. areas where a potential release would effectively impact these sensitive targets in a matter of minutes. Policing and surveillance can consequently focus and block-off the main risk areas during large sporting events, other large gatherings of people and protect sensitive infrastructure in cities.

11.2.3 Air Pollution from Elevated Point Sources

Above the UCL, most of the multitude of emission sources from the urban landscape can be treated as if they arise from lines (e.g. top of canyons or highways) or areas (e.g. dwellings and vegetation). However, there are also large point sources that can inject air pollutants directly into the surface layer above the UCL. These are mainly tall chimneys associated with industrial operations or power plants. The height of the stack is designed to ensure that contaminants are diluted by mixing in the UBL and extreme concentrations in the UCL are prevented.

To model elevated point sources well above mean building height ($z_H$), the specific arrangement of buildings and roughness elements at the urban surface can be neglected and the urban canopy can be treated simply as an extended rough surface and parameterized with an integral aerodynamic roughness length $z_0$ and zero-plane displacement $z_d$ (Section 4.3.2). It is useful to discuss this type of pollution here first, using a simple Gaussian plume model, because it illustrates how atmospheric processes govern the dispersion and dilution of contaminants. This is followed by discussion of urban-specific effects on plume dispersal.

**Gaussian Plume Models**

These are deterministic models that are applied to ‘ideal’ situations where there are continuous emissions from a point source over extensive, uniform roughness where the plume contents are usually inert. Although initially developed for open flat terrain, they can be
modified for urban situations and even incorporate some UCL effects. Gaussian plume models predict the steady-state time-averaged concentration $\chi$ at a location (given by the co-ordinates $x, y, z$) downwind from a point source. While they can assess the average concentration over a long time period, they cannot predict peak concentrations experienced at shorter, turbulent time scales. Under favourable conditions, they apply to distances in the range from a few hundred metres to a few kilometres downwind from an emission source.

Figure 11.12 illustrates the Gaussian plume model concept. A plume emerges from an elevated point source (a stack) that is continuously emitting air pollutants at a constant rate $E$ ($\mu$g s$^{-1}$). As the pollutants enter the urban atmosphere, they form a plume that is advected by the mean wind and mixed by turbulence, which regulates its spread. If one were to take a cross-section of the plume at different distances from the source, it would show that the mean pollutant concentration, averaged over a considerable time (to eliminate the random nature of turbulence), is greatest in the centre of the plume and diminishes towards its edges. This ‘bell-shaped’ distribution is well described by the Normal or Gaussian probability distribution in both the horizontal and vertical, although at different rates in the two directions. The shape emerges as the core of the plume is gradually mixed by turbulence, causing the peak concentration to fall as the cross-sectional area of the plume increases. The mathematical description of such functions allows us to model the dispersion and calculate the mean concentration outdoors $\bar{\chi}$ (in $\mu$g m$^{-3}$) of an air pollutant at any point $(x, y, z)$ downwind of a stack with height $H$ (in m):

$$
\bar{\chi}(x, y, z) = \frac{E}{2\pi \sigma_y \sigma_z u} \exp \left( -\frac{y^2}{2\sigma_y^2} \right) \left[ \exp \left( -\frac{(z - H)^2}{2\sigma_z^2} \right) + \exp \left( -\frac{(z + H)^2}{2\sigma_z^2} \right) \right] \quad (\mu\text{g m}^{-3})
$$

Equation 11.7

where $\pi$ is the mean wind speed (m s$^{-1}$), here assumed constant across the depth of the plume. The spread of the plume is regulated by $\sigma_y$ and $\sigma_z$ which are the lateral and vertical standard deviations of the concentration field, respectively, which increase with distance from the source. They can be related to the lateral ($\sigma_v$) and vertical ($\sigma_w$) standard deviations of turbulent fluctuations (in m s$^{-1}$). For example near the source ($< \approx$ approximately 1 km), the plume spreads linearly with distance $x$:

**Figure 11.12** Air pollutant dispersion from an elevated point source, modelled using a Gaussian dispersion model (Modified after: Turner, 1970).
\[ \hat{\sigma}_y \approx \frac{X \sigma_y}{H} \text{ and } \hat{\sigma}_z \approx \frac{X \sigma_z}{H} \]

Equation 11.8

Far from the source (> approximately 1 km), the plume spread changes to square-root with distance. The last term on the right-hand side of Equation 11.7 is included to account for the increased concentration at positions downwind of the point at which the plume has already ‘touched’ the ground. In this formulation it is assumed that all of the pollutant is folded back up into the atmosphere and none is deposited, an assumption called ‘eddy reflection’.

In most cases, we are interested in concentrations at ground level, where people live. For this, Equation 11.7 can be simplified to predict concentrations at ground level (i.e. \( z = 0 \)).

\[ \chi(x, y, 0) = \frac{E}{\pi \hat{\sigma}_y \hat{\sigma}_z} \exp \left( -\frac{y^2}{2 \hat{\sigma}_y^2} - \frac{H^2}{2 \hat{\sigma}_z^2} \right) \left( \text{\( \mu g \) m}^{-3} \right) \]

Equation 11.9

It is worth pointing out some of the controls on the predicted pollution concentration at any location in these formulations. First, \( \chi \) at any point is directly proportional to the source strength (i.e. \( \chi \propto E \)) and inversely related to the mean wind speed (i.e. \( \chi \propto \pi^{-1} \)), see Figure 11.3. Second, \( \chi \) is inversely related to the TKE (i.e. \( \chi \propto (\hat{\sigma}_y \hat{\sigma}_z)^{-1} \), which is controlled by stability). Instability encourages vertical spread, whereas stable conditions have a restraining influence. Third, \( \chi \) at ground level at a given distance downwind is decreased by raising the effective stack height \( H \). Other things being equal, higher point sources cause lower concentrations at the ground downwind, because turbulent mixing will have had longer to dilute the plume contents. Tall stacks are therefore usually of help in combating poor air quality near the point of release, although the total mass emitted does not change. The effective height of release can also be increased if the effluent emerges at a high velocity, and at a temperature well above that of the environmental air temperature so that the plume possesses buoyancy and rises higher. The plume then ascends well above the stack exit before bending-over and proceeding downwind.

Generally, Gaussian dispersion models try to account for urban effects by adjusting \( \hat{\sigma}_y \) and \( \hat{\sigma}_z \). Compared to typical rural areas, \( \hat{\sigma}_y \) is about two times larger, and \( \hat{\sigma}_z \) is 2 to 5 times enhanced over a city. Many Gaussian dispersion models include specific urban parameters and may have modifications to represent urban effects on flow and dispersion. Processes considered are lateral shifting of the plume centrelines due to plume channelling along the dominant canyon axes in relation to mean wind speed (Theurer et al., 1996), simple building and downwash effects, and traffic-produced turbulence (Section 4.2.3). Some models allow users to input building dimensions to calculate the trapping of air pollutants in building wakes and urban canyons.

**Plume Dispersal Characteristics in the Urban Boundary Layer**

At the scale of plumes from elevated sources, cities are rarely homogeneous and changes in roughness and thermal surface characteristics are the norm. Figure 11.13 illustrates the behaviour of various plumes that are within, or cross transitions between, rural and UBLs. At the left a rural stack plume is emitted into a stable nocturnal inversion layer, with very little dispersive capability in the vertical. It can stay as a narrow concentrated ‘pipe-like’ plume with little dilution in any direction or it can oscillate lazily sideways forming a ‘fan-shaped’ thin sheet (plume form: fanning). Upon entering the UBL the same plume encounters greater turbulent activity, due to the UHI and increased roughness. As a result it is rapidly mixed, especially down towards the RSL and surface, it fumigates the UBL (plume form: fumigation). An elevated plume emitted fully within the UBL usually enters an approximately neutral, well-mixed layer and disperses roughly equally well vertically and horizontally (plume form: coning). At the right, downwind of the city, an elevated source is

![Figure 11.13](https://www.cambridge.org/core/core/terms.https://doi.org/10.1017/9781139016476.012)
able to disperse easily in the lower part of the UBL but is largely prevented from mixing down due to the newly developing rural stable layer (plume form: lofting). For surface-based receptors the fanning case is temporarily good, but in the morning the surface inversion is eroded and fumigation happens. For as long as it lasts, which often is not very long, the lofting plume form is best for surface-based receptors such as people.

### 11.3 Urban-Scale Air Pollution

At the scale of a city with its many emission sources individual smaller plumes lose their identity and contribute to a more general contamination of the whole UBL. The efficiency of turbulence at this scale produces a relatively homogeneous mélange of contaminants that fill the depth of the ML.

Table 11.3 lists typical long-term (annual) average concentrations of major air pollutants in remote, rural, and urban atmospheres together with current annual and short-term guideline values for each air pollutant as set by the WHO. WHO guidelines offer advice to authorities in charge of air quality to protect human health, they are appropriate for all global regions. Individual countries can set their own standard values for management and enforcement. The concentration of air pollutants in the UBL of cities is substantially greater than in the ABL of remote areas. What these figures do not capture is the temporal variation that is largely a result of changes in the state of the atmosphere and in rates of emission (winter vs summer, weekends vs weekdays, and diurnal profiles of traffic and human activity). The following section first examines controls on urban-scale air pollution before considering the relevant chemical processes that lead to secondary pollutants. Finally, the role of urban-scale air pollution modelling as an operational forecasting and management tool is considered.

#### 11.3.1 Meteorological Controls on Air Quality in the Urban Boundary Layer

For illustrative purposes, we formulate a simple model to predict the average concentration $\overline{\chi}$ (in μg m$^{-3}$) of an air pollutant in the UBL (Figure 11.14). Here the UBL is divided into boxes arranged sequentially along the path of the ambient wind. The top of the boxes corresponds to the height of the ML ($z_i$) (Section 2.2.1). The urban surface emits air pollutants from below into the boxes at an average flux density $F_p$ at the surface (μg m$^{-2}$ s$^{-1}$). Pollutant removal from the volume is possible via settling and deposition at the surface (Section 11.1.3), through chemical reactions, or through advection by the mean wind (m s$^{-1}$) averaged over the depth $z_i$. For simplicity, removal and chemical reactions are neglected so the conceptual model applies only to relatively unreactive air pollutants that do not settle or are deposited in the urban area.

Further — to simplify discussion — air entering the domain from the left is assumed to be clean, the pollutant is thoroughly mixed over the depth $z_i$. Lateral mixing, perpendicular to the mean flow direction, is considered to be instantaneous. In this situation we can write that any distance $\Delta x$ (m) from the upwind boundary of the city the concentration of an air pollutant $\overline{\chi(x)}$ is given from:

#### Table 11.3

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Remote background ABL</th>
<th>Typical rural ABL</th>
<th>Typical UBL (μg m$^{-3}$)</th>
<th>WHO annual guideline</th>
<th>WHO short-term guideline</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>60–150 μg m$^{-3}$</td>
<td>150–500 μg m$^{-3}$</td>
<td>200–1,500 μg m$^{-3}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>~ 3 μg m$^{-3}$</td>
<td>3–40 μg m$^{-3}$</td>
<td>20–200 μg m$^{-3}$</td>
<td>40 μg m$^{-3}$</td>
<td>200 μg m$^{-3}$ (1-h mean)</td>
</tr>
<tr>
<td>O$_3$</td>
<td>40–70 μg m$^{-3}$</td>
<td>30–100 μg m$^{-3}$</td>
<td>20–90 μg m$^{-3}$</td>
<td>-</td>
<td>100 μg m$^{-3}$ (8-h mean)</td>
</tr>
<tr>
<td>PM2.5</td>
<td>5–30 μg m$^{-3}$</td>
<td>10 μg m$^{-3}$</td>
<td>25 μg m$^{-3}$ (24-h mean)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PM10</td>
<td>10–50 μg m$^{-3}$</td>
<td>20 μg m$^{-3}$</td>
<td>50 μg m$^{-3}$ (24-h mean)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO$_2$</td>
<td>0–0.5 ng m$^{-3}$</td>
<td>0–20 μg m$^{-3}$</td>
<td>0–50 μg m$^{-3}$</td>
<td>-</td>
<td>20 μg m$^{-3}$ (24-h mean)</td>
</tr>
</tbody>
</table>
\[ \chi(x) = \frac{F_p \Delta x}{\pi z_i} \quad (\mu g \text{ m}^{-3}) \quad \text{Equation 11.10} \]

This relationship, although very simplified, reveals a number of fundamental dependencies and suggests potential air quality management options:

- The stronger the flux of air pollutants at the surface \( (F_p, \text{i.e. rate of emissions per unit area}), \) the greater the resulting \( \chi \) in the UBL. Although obvious, this reminds us that emission reduction is the single most effective management action to improve urban air quality, and it represents a direct approach to addressing the problem at the source.

- The concentration is inversely related to the depth of the UBL \( (z_i) \). When \( z_i \) is small, it defines a shallow UBL so \( F_p \) is mixed into a smaller volume and \( \chi \) increases. This depth cannot be regulated, but \( z_i \) is generally larger during daytime, and lower at night. Further, \( z_i \) is larger over cities than rural areas owing to increased roughness (Chapter 4) and the UHI (Chapter 7). This should benefit urban air quality.

- \( \chi \) increases linearly with distance of travel \( (\Delta x) \) across the urban area as the wind advects air pollutants from upwind sources resulting in higher concentrations downwind. This implies that to reduce population exposure to degraded air quality in the city, additional polluting industries and infrastructure should, in most scenarios, be sited on the dominant downwind side of the urban area. However, if the less frequent flow from the opposite direction typically coincides with strong stability and low \( z_i \), this can cause industrial emissions to flow back into the city and cause unfavourable concentrations (see also Section 15.4.3).

- \( \chi \) is inversely related to mean wind speed \( (\bar{u}) \). Higher \( \bar{u} \) means greater flushing and lower concentrations. This is analogous to the case of a single plume, as illustrated in Figure 11.3. Although over the depth of the UBL \( \chi \) cannot be controlled, there are two management implications: (i) \( \chi \) will be worse when \( \bar{u} \) is small, and (ii) cities situated in wind-sheltered topographies (valleys, mountain basins) are generally more prone to periods of high \( \chi \) compared to those exposed to strong winds. There are also design considerations at the local- to mesoscale to maintain higher winds and disperse air pollutants.

The ventilation factor \( (V_f = \pi z_i) \) combines the two atmospheric controls in Equation 11.10 and provides a simple means to assess the capacity of the box to disperse and dilute emissions. Generally, periods of poor air quality occur when \( V_f \) is smallest, and emissions \( E \) are largest. \( V_f \) tends to exhibit strong diurnal and seasonal variations related to UBL development and synoptic meteorological controls. Other things being equal, \( \bar{u} \) is characteristically stronger in daytime and so is \( z_i \), due to convective growth of the ML (Figure 2.12). So, the components of \( V_f \) are correlated such that the best environment for dispersion usually occurs by day and the poorest by night.

### 11.3.2 Smog

Smog refers generally to the phenomena of degraded air quality on urban to regional scales. The air is visually changed appearing variously dirty, hazy,
discoloured and may have a noticeable odour. Periods when smog persists and air quality in the UBL progressively deteriorates, to the point where it becomes a public health issue, are termed ‘air pollution episodes’. There are two classes of smog.

**Sulphur-Based Smog**

The term ‘smog’ was originally coined to describe a mixture of smoke and fog that characterizes the UBL in cities with high PM and SO$_2$ emissions derived from the burning of coal, solid fuels and sulphurized petroleum. This sulphur-based smog is characteristic of urban systems with a high density of emissions from open fires, furnaces and uncontrolled emissions from industry and power generation that use these fuels. In a very humid atmosphere particulates grow in size by absorption of vapour and some form CCN on which droplets form. The primary pollutant SO$_2$ is absorbed into droplets, where it oxidizes to sulphur trioxide (SO$_3$), which reacts with water vapour in the presence of catalysts to form sulphuric acid (H$_2$SO$_4$). Since acids have an affinity for water they allow droplets to grow further hygroscopically and cause haze. Conditions ideal for the formation of sulphur-based smog occur in mid- to high latitudes in winter when emissions for space heating are substantial.

The London, United Kingdom smog episode in December 1952 is a case in point. Under cold and stable weather, fuel consumed for space heating resulted in high emissions of SO$_2$ and PM. Chimney smoke from myriad domestic fireplaces, mainly burning coal, fumigated the UCL across the city. Such was the density of the smog that sunshine could not penetrate to warm the underlying surface, inhibiting mixing and growth of the ML by thermal turbulence – which along with weak winds caused a very low $V_f$. The air pollutant concentrations exceeded modern standards by an order of magnitude for several days and resulted in 12,000 ‘excess’ deaths (Bell and Davies, 2001) (i.e. when compared with the expected number of deaths in this period).

Figure 11.15 shows seasonal average concentrations of SO$_2$ and PM measured in Dublin, Ireland, over a twelve-year period. In the first half of this series, the use of poor quality bituminous coal to heat homes that was still widely common in the high winter season caused frequent sulphur-based smog episodes. In 1990, the city banned the marketing, sale and distribution of bituminous coal, which saw a dramatic improvement in air quality as it did in London. An epidemiological analysis of death rates indicates about 243 fewer cardiovascular and 116 fewer respiratory deaths per year after the ban on coal sales (Clancy et al., 2002). Even today, sulphur-based smogs remain common in many cities where coal is a primary fuel.
Photochemical Smog

Serious air quality episodes have plagued the metropolitan area of Los Angeles, United States, since the 1940s. At first, industrial sources were blamed, and the air pollution was attributed to sulphur compounds, but in the early 1950s, chemist Arie Haagen-Smit showed photochemical processes are relevant when emissions from gasoline combustion are converted into the secondary pollutant ozone (O₃). This photochemical smog needs strong sunlight for certain chemical reactions to occur. Photochemical smogs occur in many urban areas, but because of the requirement of strong irradiance their occurrence outside the tropics tends to be restricted to the summer season. Under typical anticyclonic conditions with clear skies that characterize photochemical smogs, air quality is further degraded because low wind speeds and subsidence inversions cause a low flow. The net result is a hazy atmosphere with a brownish colour, greatly reduced visibility and distinctive odour. Photochemical smog can irritate the eyes and the respiratory tract (e.g. reduce lung capacity, aggravate asthma) and cause plant damage (e.g. injure tissue and reduce yield).

The principal emissions responsible for the formation of O₃ in photochemical smog are NOx and VOCs. Internal combustion engines using gasoline are the primary source of these emissions. VOCs are also emitted through fugitive and evaporative emissions from solvent use and from the biosphere (Section 11.1.1).

The formation of ozone from NOx in the UBL is governed by the cycle in Figure 11.16 in the shaded box of the top part. The energy supplied by photons of UV radiation can photodissociate NO₂ into nitric oxide (NO) and an atomic oxygen radical (O):

\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}. \]  
(R1)

Here, \( h\nu \) is the energy of a photon, where \( h \) is the Planck constant and \( \nu \) is its wave frequency (in \( \text{s}^{-1} \)). The photolytic rate \( j_1 \) of reaction R1 (in \( \text{s}^{-1} \)) is directly proportional to the intensity of UV radiation in the wavelength range 0.37–0.42 \( \mu \text{m} \). R1 is hence limited to daytime situations, and \( j_1 \) is usually strongest at noon. The oxygen radical resulting from R1 is highly reactive and combines immediately with the ambient molecular oxygen (O₂) to form ozone (O₃):

\[ \text{O} + \text{O}_2 + M \xrightarrow{k_2} \text{O}_3 + M \]  
(R2)

where \( M \) is another molecule involved in absorbing some of the surplus energy (not in Figure 11.16); in most cases this is simply the abundant O₂ or N₂. The O₃ formed then reacts with NO to yield again NO₂ and O₂:

\[ \text{O}_3 + \text{NO} \xrightarrow{k_1} \text{NO}_2 + \text{O}_2 \]  
(R3)

\( k_2 \) and \( k_3 \) are the kinetic rates for O₃ formation and O₃ destruction, respectively (in \( \text{s}^{-1} \)). The cycle described by reactions R1 to R3 leads to a theoretical equilibrium between NO₂, NO and O₃, which is a photolytic steady-state called the Leighton relationship:

\[ [\text{O}_3] = \frac{j_1 [\text{NO}_2]}{k_3 [\text{NO}]} \]  
Equation 11.11

The Leighton relationship results from the assumption that O₃ and NO are formed and destroyed continuously with no net production over time. The ratio of \([\text{NO}_2]/[\text{NO}]\) sets a limit on [O₃] and is therefore a key parameter to assess ozone formation potential.

Predicted urban [O₃] based on the Leighton relationship would yield only \( \sim 0.01 \mu \text{g} \text{ m}^{-3} \) under typical urban situations, but observations show values can reach 100 \( \mu \text{g} \text{ m}^{-3} \) (see Figure 11.18). Such high concentrations cannot be explained by the Leighton relationship alone, they are due to a complementary set of reactions that convert NO to NO₂ without depleting O₃. This is enabled by the simultaneous presence of VOCs in urban air. Select VOCs can oxidize NO to NO₂ hence leaving the O₃ previously formed by R1 and R2 unaffected and reduce the probability of R3. This is illustrated by the set of reactions in the lower part of Figure 11.16 (in red) which can run several times (hence they are a catalytic cycle) and replenish the NO₂ reservoir without destroying an equivalent amount of O₃.

For example, in reaction R4, a methyl radical (CH₃) is formed from the simplest hydrocarbon, methane (CH₄), reacting with the hydroxyl radical (OH). The methyl radical then reacts with oxygen in R5 and the resulting methyldioxy radical can oxidize NO to NO₂ and form a methoxide radical (R6). That radical then reacts with O₂ (R7) to form two hydroperoxyl radicals (HO₂) and formaldehyde (HCHO).

[1] Square brackets are a short-hand notation for the concentration of the pollutant.
At that point the reactions can follow one of two paths. If R8 occurs, HO₂ will oxidise another NO molecule and produce a hydroxyl radical (OH):

\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \quad \text{(R8)} \]

that in turn reacts with another hydrocarbon (through R4) thus closing the catalytic cycle and allowing R4 to R8 to repeat. The net effect of this catalytic cycle is to destroy hydrocarbons while creating formaldehyde that increases its concentration in photochemical smog and oxidizing NO:

\[ \text{CH}_4 + 2\text{O}_2 + 2\text{NO} \rightarrow \text{H}_2\text{O} + 2\text{NO}_2 + \text{HCHO} \quad \text{(R4-R8)} \]

Increasing concentrations of formaldehyde in urban air, as a result of this cycle, are partly responsible for the distinctive odour of photochemical smog. Note that R4 to R8 do not consume OH, rather OH is ‘recycled’ – it is the catalyst, and none of these reactions require UV radiation, so they can occur day and night.

Alternatively, the two HO₂ molecules, formed in R7, can combine via R9 to create hydrogen peroxide (H₂O₂) and oxygen:

\[ \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad \text{(R9)} \]

This breaks the catalytic cycle and terminates the role of the hydrocarbon molecule in ozone formation.

Figure 11.16 shows only one possible pathway, based on the methyl radical (CH₃). Similar reaction cycles are possible with longer and more complex hydrocarbon radicals. A relevant case is the acetyl radical (CH₃CO), which can fuel the cycle with...
additional CH₃ and form the peroxyacetyl radical (CH₃COO₂) that reacts with NO to form the vapour of peroxyacetyl nitrate (PAN), which also builds up in urban air as a product of the cycle over time. Similar to formaldehyde, PAN is an important compound in photochemical smog accompanying high O₃ concentrations. Like O₃, PAN is a major eye and throat irritant and damages plants.

In summary, to build-up high concentrations of the secondary pollutants O₃, formaldehyde and PAN and in the UBL we need:

- **High [NOₓ]**, derived primarily from vehicle emissions in urban air.
- **Reactive VOCs** – also emitted from vehicles plus evaporative emissions that are temperature dependent from other anthropogenic and biogenic sources.
- **Sufficient high-energy UV radiation** to enable a substantial j in R1, this is typically found in anticyclones with ample solar irradiance.

Only if all three prerequisites are fulfilled, will the secondary pollutants O₃, formaldehyde and PAN be formed. Photochemical smog is hence characteristic for urban areas with NOₓ (primarily vehicles) and VOC emissions (vehicles, fugitive and biogenic emissions) that build-up under anticyclonic conditions with ample irradiance under weak winds.

**Temporal Dynamics of Photochemical Smog**

The daily change in both emissions due to human activity (e.g. traffic patterns) and of solar UV radiation combine to create characteristic traces of both the primary and secondary pollutants involved in photochemical smog. The typical course of measured air pollutant concentrations over a summer day is illustrated in Figure 11.17 in the city of Essen, Germany. The early morning rush-hour adds [NOₓ], in particular [NO] which results in a molar [NOₓ] / [NO] ratio of ~1. The abundant [NO] means the net formation of [O₃] remains low during rush hours. With increasing shortwave irradiance, [O₃] forms at higher rates and when emissions cease in the later morning, the reservoir of [NO] is used up quickly. By about 1100 h, the build-up accelerates and high [O₃] is present in the urban atmosphere during the afternoon, while primary pollutants are lower. The afternoon is also the time of highest surface and air temperature, so anthropogenic and biogenic fugitive emissions of VOCs, that are temperature dependent, peak. A second burst of NOₓ emissions is caused by the evening rush-hour, but this is not clearly visible in Figure 11.17 because of the strong mixing of the UBL at that time. The onset of darkness inhibits further formation so [O₃] decays in the evening and is completely destroyed by 2300 h. Interestingly, there is a secondary nocturnal maximum of [O₃] at 0200 h, associated with an increase in wind and mixing. Such nocturnal secondary maxima are a common feature and cannot be explained by chemical formation, because there is no shortwave irradiance to drive R1. Instead, such secondary maxima are due to air masses still rich in [O₃] that are transported back into the city and down to the surface. These nighttime increases are generally attributed either to mixing of [O₃] rich air from the residual layer downwards, when the nocturnal inversion temporarily breaks down, or by advection in from rural areas outside the city, by the urban heat island circulation (UHIC, Section 4.4). In both cases, the rural boundary layer and the residual layer generally have a higher [NOₓ] to [NO] ratio, which causes [O₃] to be less quickly depleted overnight.

**Intra-Urban Patterns of Photochemical Smog**

Figure 11.18 shows midday [NO], [NOₓ] and [O₃] measured by a mobile laboratory that traversed through different neighbourhoods of Essen. The values are averaged over many summer days. Data has been grouped into that measured along motorways, main and secondary roads, and in residential and green areas. Along motorways abundant primary pollutants inhibit O₃ accumulation. There, [NOₓ] is...
high and the molar \([\text{NO}_2] / \text{[NO]}\) ratio is low (~0.1), which means that \([\text{O}_3]\) once formed is immediately depleted by \([\text{NO}]\) (Equation 11.11). In places where primary pollutant emissions are lower, for example along less busy secondary roads, the higher molar \([\text{NO}_2] / \text{[NO]}\) ratio (~0.4) and plentiful \([\text{VOC}]\) causes \([\text{O}_3]\) to climb, yet highest \([\text{O}_3]\) is found in residential and green areas of the city where molar \([\text{NO}_2] / \text{[NO]}\) is ~0.7. On regional scales, photochemical smog often causes \([\text{O}_3]\) to peak in rural areas several 100s of kilometres downwind of cities. These regional patterns in the urban plume are discussed in more detail in Section 11.4.1.

**Implications for Air Quality Management**

The reaction pathway taken after R7 (that is, whether R8 or R9 dominates), is an important ‘switch’ in the cycle, and depends on the concentration of NO. If there is a plentiful supply of \([\text{NO}]\) but little \([\text{VOC}]\), R8 is more likely to happen, the cycle continues and more ozone is formed. In the reverse situation where there is little \([\text{NO}]\) but plentiful \([\text{VOC}]\) there are more \(\text{HO}_2\) radicals in the atmosphere, R9 dominates and the cycle terminates. Other reactions, such as between \(\text{HO}_2\) and the methyldioxy radical, also end the reaction sequence. These ‘side tracks’ have implications for regulating \([\text{O}_3]\) concentration, which is a function of both \([\text{VOC}]\) and \([\text{NO}_x]\) concentrations (Figure 11.19). Generally, with higher \([\text{VOC}]\) and \([\text{NO}_x]\) concentrations, concentrations of \([\text{O}_3]\) increase. The maximum \([\text{O}_3]\) concentration that can be reached, however, depends on the ratio of \([\text{VOC}]\) to \([\text{NO}_x]\). At intermediate ratios (4:1 to 10:1) conditions for \([\text{O}_3]\) formation are most favourable. A closer look at Figure 11.19 shows two particular régimes, depending on the ratio \([\text{VOC}]\) to \([\text{NO}_x]\), that are relevant to the management of \([\text{O}_3]\) in urban environments:

- **VOC limited régime** (also called: high \([\text{NO}_x]\) régime): The catalytic cycle R4 to R8 flourishes, consuming some of the abundant NO and hence inhibiting partially the destruction of \([\text{O}_3]\). The high availability of \([\text{NO}_x]\) means R9 is unlikely to
happen. \([\text{O}_3]\) is most sensitive to the availability of VOCs. Higher VOC emissions would mean more \(\text{O}_3\), while increasing NO\(_x\) emissions alone would not change much.

- **NO\(_x\) limited régime** (also called: low [NO\(_x\)] régime):
  The lack of NO means reaction R9 is more likely to happen, and the catalytic cycle of the VOCs is less effective. At the same time the limited [NO\(_x\)] means little \(\text{O}_3\) destruction and production by reactions R1 to R3. \([\text{O}_3]\) is most sensitive to the availability of NO\(_x\). Increasing NO\(_x\) emissions would therefore cause more \(\text{O}_3\), while higher VOC emissions alone would not yield much change to \(\text{O}_3\) concentrations.

The UBL above city centres tends to have a VOC limited régime because there are high [NO\(_x\)] emissions from traffic. Here a reduction of NO\(_x\) alone may actually worsen \(\text{O}_3\) pollution (path A1, in Figure 11.19), and a reduction of VOC, or both NO\(_x\) and VOC in the city is the proper action to reduce \([\text{O}_3]\) (path A2). But reducing VOC emissions is difficult to implement because there are multiple small-scale sources (e.g. solvents, paints, trees) that are not as easily regulated as vehicles, which are the main source of NO\(_x\).

Often the highest \([\text{O}_3]\) are found in rural areas downwind of cities (Figure 11.22), which are NO\(_x\) limited régimes, with ample VOCs (partially derived from biogenic emissions). Here, reducing emissions of NO\(_x\) upwind will often lower \([\text{O}_3]\) (path B1, in Figure 11.19). Reducing VOC emissions alone will have little effect (path B2).

This situation shows the counter-intuitive effect of certain actions: reducing NO\(_x\) emission (e.g. by traffic restrictions) benefits communities downwind, but may worsen conditions in the city centre if not accompanied by a simultaneous decrease in VOC emissions. The specific situation depends on the regional emission composition, climate and wind field – so management actions to reduce \(\text{O}_3\) do not necessarily affect all parts of an urban region the same way and need to be planned carefully. Hence, management of air quality involving photochemical smog is usually guided by numerical model simulations.

### 11.3.3 Modelling Urban Air Pollution

Numerical air quality models at urban- to regional scales are necessary tools to forecast air quality and to guide emission management strategies. Generally such models combine a representation of atmospheric dynamics, atmospheric chemistry and urban emission inventories in a physically-based form to predict air pollutant concentrations in space and time.

#### Modelling Atmospheric Dynamics

Gaussian plume models (Section 11.2.3) do not take into account the complex flow field and spectrum of time scales involved in urban-scale air pollution. **Eulerian** and/or **Lagrangian** approaches (Section 3.3.1) are needed to model the dispersion and transformation of emissions at urban scales. An early attempt to run time-dependent 3-D air quality forecasts for a city was the pioneering ‘Urban Airshed Model’ developed for the Los Angeles Metropolitan Area in the early 1970s (Scheff and Morris, 1993). The model solved atmospheric dispersion in a simple Eulerian grid, using conservation equations for several air pollutants and selected key chemical transformations. Today, a large number of such **photochemical grid models** (PGM) are available, and at much finer resolution, and with improved sophistication. PGMs can model airflow and pollution dispersal not only for a domain of a single city, but for entire urbanized regions and continents. PGMs also account for radiation exchanges using the specific wavelength bands needed for photochemical reactions, and predict temperatures that control meteorological processes and the rate of chemical reactions. PGMs are used in prognostic modes to forecast pollutant concentrations, to inform regulatory measures (i.e. identify effective emission reduction scenarios) and for research purposes.

#### Modelling Atmospheric Chemistry

For computational reasons, it is not possible to incorporate the thousands of reactions of each possible air pollutant. In particular the treatment of the large variety of VOC species is a challenge in PGMs. Therefore, VOCs are often grouped into simple classes of similar reactivity, which are usually olefins, paraffins, aldehydes and aromatics. These classes still require several hundred chemical equations to be solved at each grid node and time step of the model. The corresponding kinetic and photolytic rates for individual reactions are based on many laboratory chamber measurements and are functions of temperature and radiation that are taken from the dynamical part of the model.
Emission Inventories

The description of emissions are the single most sensitive input to modern PGMs. Emission inventories are geographical databases that describe the location, timing, quantity and chemical composition of primary pollutants emitted in a city or region. The inventories are coupled to the model as one of the lower boundary conditions. Emission inventories are needed to model primary pollutant concentrations and therefore are also critical to the accurate prediction of secondary pollutants.

For convenience, we should first categorize emissions into three major physical processes: (i) combustion and industrial; (ii) evaporative and fugitive emissions, and; (iii) biogenic emissions (Section 11.1.1). Combustion sources are further separated into: traffic (road, rail, ship, air); domestic and commercial buildings due to space heating and cooling, hot water demand and appliances, and industry and power generation. The emissions from each of these sources follow distinct diurnal, weekly and seasonal patterns associated with the rhythms of the urban metabolism (e.g. commuting to and from work, heating and cooling at work and home and economic production cycles). Sources of evaporative and fugitive emissions (as well as biological emissions) are more diffuse in nature and are controlled in some cases by temperature and other environmental or technological controls. In particular, evaporative and biogenic VOC emissions are difficult to estimate.

Urban-scale emission inventories are constructed based on top-down or bottom-up approaches. These are directly analogous to the means by which the anthropogenic heat flux ($Q_F$) is estimated (Section 6.2). The top-down approach uses fuel consumption statistics available at coarse (e.g. national or regional) scales and down scales them to a specific urban area. Because the exact location of fuel combustion is not known or is not accessible, these data are distributed spatially and temporally using proxy data, such as population density. Similarly, yearly data may be decomposed to a finer temporal scale using traffic counts, or seasonally using heating degree-days (HDD). The strength of the top-down modelling approach is that total emissions over longer time scales are quite robust. However, there is uncertainty about downscaling, i.e. when and where emissions are released in an area or within an urban area.

The bottom-up approach derives emissions from knowledge about a small number of typical urban elements such as buildings, vehicles or trees. Emissions from those generic ‘elements’ of the urban metabolism can be modelled using sub-models such as building energy models, traffic flow models or plant physiological models. Total emissions from an area are aggregated to the scale of interest (grid cell, block, neighbourhood, city) using a known spatial distribution of those elements. Many cities have access to detailed databases or geographic information systems, which allow detailed identification of buildings, roads or green space, thereby enabling and assisting the modelling of emissions. A bottom-up approach has the advantage of functionally and/or physically modelling the urban metabolism, associated fuel combustion and air pollutant emissions. This may allow the construction of inventories for scenarios that reflect plans for changes in urban form, the mix of land uses and technology. However bottom-up inventories are sensitive to the modelling assumptions, and small errors in the sub-models propagate into larger uncertainties at the urban scale.

Emission inventories should also separate between emissions that happen within the domain or grid cell of interest (local emissions) and emissions caused by the domain or grid cell but released outside (external emissions). The concept of external emissions is illustrated by the consumption of electricity for heating and lighting. Electricity may be generated outside the grid cell or area of study and be delivered to the city via a grid system. Finally, there are many urban-located functions, such as air and sea transport that generate emissions but are difficult to attribute to any one place.

In practice, scaling bottom-up inventories to match fuel consumption data from top-down approaches at a coarser scale can be a successful strategy to benefit from the advantages of the two emission inventory approaches, i.e. realistic total regional emissions as well as a functional understanding of the system in terms of its detailed spatio-temporal distribution.

Figure 11.20 shows a detailed emission inventory for NOx, SO2, VOC and PM10 derived by a combination of top-down and bottom-up methods for the greater London, United Kingdom area. The maps illustrate the characteristic geographic distributions resulting from the relative importance of emission sectors. The inventory map for NOx (Figure 11.20a)
reflects the road network with motorways and arterial roads being the ‘hot-spots’. In contrast the emission map of \( \text{SO}_2 \) (Figure 11.20b) only weakly identifies with the urban area. Emissions are tied to a few strong point sources for fuel processing, ship tracks, rail and air transportation, such as four major airports. Emissions of VOCs are even more diffuse in space (Figure 11.20c) and their variation is related to

**Figure 11.20** Maps of modelled primary pollutant emissions for the Greater London Area, UK at 1 km\(^2\) resolution for the year 2009. The maps show: (a) nitrogen oxides, \( \text{NO}_x \) expressed as \( \text{NO}_2 \), (b) sulphur dioxide, \( \text{SO}_2 \), (c) volatile organic compounds, VOCs (excluding methane) and (d) particulate matter < 10 \( \mu \text{m} \) in diameter. The charts underneath of each map describe the contribution of various sectors to the total emissions in the map domain (Source: Maps drawn based on data provided in UK’s National Atmospheric Emissions Inventory, NAEI, Department for Environment, Food and Rural Affairs, UK Government).
various land cover – primarily settlements (solvent use). Particulates (Figure 11.20d) again reflect a complex mixture, where the road network is a primary location for emissions.

The link between fuel/energy use and emissions is provided by emission factors that relate the mass of air pollutant released to the mass of fuel burned (or to distance driven). These are necessary for both top-down and bottom-up inventories yet are often associated with high uncertainties. They depend on the fuel type and its composition, on the design of the internal combustion engine, and the conditions during the combustion process (temperature etc.). Depending on the combination, a range of values is possible. There are reports and online databases which summarize emission factors for specific sources, practices and economic systems.

11.4 Regional and Global Effects of Urban Air Pollution

Full treatment of urban air pollution chemistry and meteorology requires that we cannot simply look at a city in isolation. Many air pollutants emitted in cities are transported far beyond the city’s limits where they are still able to affect human health and ecosystems, or even cause large-scale and long-term disturbance to the global climate system. Managing medium to long-lived air pollutants involves regional (transboundary) and global (international) efforts and solutions.

11.4.1 Urban Plumes

At the meso- to macroscale, cities appear as large ‘point’ sources with their plume extending many hundreds to thousands of kilometres downwind. The persistence of such plumes depends on both the residence time of its constituents (see Figure 11.5) and the degree of mixing that a plume experiences. If conditions are suitable, an identifiable mass of ‘urban’ air can be transported over great distances. Stohl et al. (2003) employed a numerical model to trace the precise origin of air pollutants reaching Europe that were emitted over North America. The study identified contributions from a number of sources, for example the urban plume produced by the metropolitan area of New York was clearly distinguishable.

The Extent of Individual Urban Plumes

Recent developments in satellite remote sensing make it possible to map air pollutant concentrations in urban plumes. Figure 11.21a shows a composite of column total NO2 recorded by means of passive satellite spectroscopy over the Middle East (Beirle et al., 2011). The column total is expressed as the number of molecules from the ground to the top of the troposphere per column ground area (m⁻²), but note that most NO2 is found in the atmospheric boundary layer.

The Middle East, due to the low frequency of cloud cover, is a preferred region for satellite-based remote sensing of air pollutants. Due to its relatively short atmospheric residence time, the mapped NO2 is found in proximity to heavily urban and industrial centres. The case of the Riyadh, Saudi Arabia — an isolated city, dominated by emissions from oil-related industries — is enlarged in Figure 11.21b. Average satellite-measured column totals of NO2 are shown for a 375 by 375 km region centred on Riyadh and conditionally sorted by wind direction. The maps illustrate the extent and persistence of Riyadh’s urban plume affecting areas downwind changing with wind direction. The NO2 plumes in all cases have a limited geographical extent of about 200 km, beyond which they approach background concentrations. Generally, the extent of the plumes is determined by source strength, wind speed, mixing and the rates of deposition and chemical transformations for an air pollutant.

Air pollutants in urban plumes undergo transformation as the polluted air travels downwind from a city. Tulet et al. (1999) studied the photochemistry of the plume of Paris, France, during a four-day air pollution episode in July 1996. Hourly O3 concentrations in the core area of Paris and upstream from Paris were considerable, but not extreme (< 100 μg m⁻³), however, rural stations located 25 to 110 km downwind of the city experienced seriously high O3 concentrations (> 200 μg m⁻³), see Table 11.3). The study linked the high rural O3 concentrations to emissions in Paris, by numerical modelling of the airflow and chemistry with a PGM at the regional scale (Figure 11.22). O3 precursors, such as NOx, experience highest concentrations over the city and! about 50 km downwind in the plume (Figure 11.22a). During transport by the plume,
precursors are chemically transformed to O₃, which peaks about 100 km downwind of the city centre (Figure 11.22b). The modelled plume processes are supported by measurements — there was a time-lag in observed O₃ maxima between measurement sites closer to Paris and those further away. The lag was between the peaks of the diurnal trace of anthropogenic emissions due to the timing of the rush hours.

Figure 11.21 Composite of average total column NO₂ measured by satellite (Ozone Monitoring Instrument on the ‘Aura’ spacecraft) at a spatial resolution of ~15 × 25 km, (a) the Middle East under low wind conditions. (b) Enlargement of the city of Riyadh with NO₂ plumes for different wind directions (Source: Beirle et al., 2011; © American Association for the Advancement of Science, used with permission).
and the time taken for the wind to advect the plume. Sites further downwind from Paris experienced O₃ maxima later in the day.

Urban–Rural Differences in Air Pollution

Although plumes of individual, isolated cities, can be identified, quantified and modelled, in most cases air pollution at the regional to continental scale is the consequence of many emission sources, where air pollutants from local sources are superimposed on those from distant urban and non-urban sources. Figure 11.23 summarizes air pollutant concentrations measured at thousands of air quality stations across Europe. The stations are classified into ‘roadside’ (adjacent to a major road or highway, Section 11.2.2), ‘urban’ (located away from traffic but in urban and suburban locations) and ‘rural’ (away from major population centres and emission sources). The curves in Figure 11.23 show the frequency distribution (histograms) of the annual average concentrations for each class. Most stations are located in central Europe, so there is a spatial bias to results.

For the three primary pollutants shown, NOₓ (Figure 11.23a), CO (Figure 11.23b) and PM10 (Figure 11.23c) roadside station concentrations are generally highest, followed by urban background and lowest at rural stations. Compared to the hemispheric background, all three primary pollutants are elevated, even in remote rural areas – in part because rural areas are not emission free, and in part because they may be located downwind of urban centres and are affected by their plumes. Note that histograms for roadside, urban and rural sites separate best for NOₓ, followed by CO, while for PM10 the differences are relatively small and the histograms mostly overlap. This is explained by the different atmospheric residence times of the species (Figure 11.5). NOₓ has a short residence time of only ~4 hours in an urban plume and hence urban–rural differences are large. CO has an average residence time of weeks to a month
and downwind areas are more affected by urban emissions. In the case of fine particulates, their long atmospheric residence time (see Figure 5.3), and also the fact that rural areas generate additional emissions (agriculture, dust) explains the tightest overlap between the three histograms.

The case of tropospheric O₃ (Figure 11.23d) is the reverse of the others – the ensemble of roadside stations experiences lowest concentrations. While O₃ is also formed from the primary pollutant NO₂, high [NO] immediately reduces O₃ back to O₂ and NO₂. Consequently, [O₃] is lower at urban sites where primary pollutants from vehicle emissions are present, while highest values are measured at rural and remote sites. Rural sites do not emit substantial amounts of NOₓ, but that advected from urban plumes to those more remote areas, along with considerable VOC concentrations, causes the build-up of high O₃ concentrations without being depleted by NO. Background O₃ concentrations in the troposphere away from urban centres have actually increased by a factor of 3–4 over the last century, due to the increase in emissions of the main precursor pollutants NOₓ and VOCs.

**11.4.2 Effects of Urban Pollutants on Ecosystems Downwind**

Air pollutants in urban plumes not only contaminate the atmosphere, but also adversely affect downwind aquatic and terrestrial ecosystems, and structures when they are deposited. Common impacts on downwind ecosystems include water and soil acidification, lake eutrophication and both fertilization and damage to agro- and forest ecosystems.

**Acidification**

Absorption of CO₂ into cloud droplets causes rain to be acidic — even in the most remote regions. In a pristine

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Caption for Figure 11.23 (cont.) (d) O₃ measured at roadside, urban background and rural sites in the European Union for the period between 2002 and 2012. Values in brackets show median values for all stations in a given category. The remote arrow denotes Northern Hemispheric background concentrations in the PBL measured at a remote site (Mace Head, Ireland). Only years with more than 75% of data coverage at each station are included (Data sources: European Environment Agency, AirBase v. 7.0 and from the Global Atmosphere Watch Program).
atmosphere, rain droplets have a pH of about 5.6. However, in an urban plume, in addition to CO₂, SO₅ and NOₓ, are also absorbed into droplets and form sulphuric acid. This further lowers the typical droplet’s pH, which can reach values as low as 2, and quite often ranges between 3 and 4 in urban plumes. If such highly acidic droplets (pH < 5.6) are deposited on the ground, built structures or vegetation, they cause damage. This is the problem of acid deposition, which is loosely referred to as ‘acid rain’. In addition to deposition by rain, acid deposition includes droplets reaching the surface as acid fog or snow or gravitational settling or dry deposition of acidic particles. Acidification has been observed in many parts of the world, especially downwind from major urban-industrial regions in Eastern North America, Europe and Asia. The acidification of soils and aquatic ecosystems can mean profound changes. Acids on surfaces and soils can corrode materials and dissolve certain rocks (e.g. limestone), further it retards decomposition of organic material in soils and affects plant health.

Figure 11.24, shows the average contribution of major urban centres in Asia to sulphur deposition on terrestrial and aquatic ecosystems. Although the urban imprint is most dominant in close proximity to urban regions, the contribution of cities is detectable at the continental scale and affects aquatic and terrestrial ecosystems thousands of kilometres away.
downwind, including the Pacific Ocean. SO₂ emissions from fuel combustion have been successfully reduced in many parts of Europe and North America, by abandoning sulphur-bearing fuels (Figure 11.15), so NOₓ and ammonia (NH₃) are now the principal acidifying components in urban plumes.

**Effects on Vegetation – Fertilization, Eutrophication and Damage**

Nitrogen is the limiting plant nutrient in mid-latitude soils, that restricts the growth potential of many terrestrial ecosystems. Inadvertent fertilization by deposition of elevated levels of NOₓ and NH₃ (or nitrogen in the form of particles) can promote vegetation growth in cities and downwind from them. The typical deposition of N downwind of cities ranges between 10 and 50 kg N ha⁻¹ y⁻¹. This can cause changes in vegetation composition, or for aquatic ecosystems can cause eutrophication (excess nutrient loading).

Trusilova and Churkina (2008) modelled the resulting changes to plant growth in ecosystems downwind of urban areas in Europe using a biogeochemical land-surface scheme. They found that both, the elevated CO₂ in urban plumes and the inadvertent fertilization by enhanced nitrogen deposition increased growth, and consequently the CO₂ uptake by vegetation. On the other hand, certain air pollutants such as O₃ or PAN; (see Section 11.3.2) are phytotoxics, that cause physiological stress, damage to leaves and reduce growth.

**Physical Changes in Weather and Climate**

Of all air pollutants, PM has the strongest impact on physical processes in the atmosphere downwind of cities where they produce a multitude of modifications. Firstly, PM changes the radiative transfer of the atmosphere by reducing shortwave and enhancing longwave radiation fluxes (Section 5.3). These effects are transferred downwind by the regional-scale plume with their magnitude depending on concentration, which in turn, depends on the residence times controlled by the size distribution of the emitted PM, the ambient wind speed and wet deposition. Secondly, PM affects droplet formation and hence cloud cover, cloud lifetime and precipitation. The role of PM as CCN, the effects of number densities and composition on cloud-life-times, and precipitation downwind of cities, are discussed in Chapter 10.

Some urban air pollutants have exceptionally long residence times in the atmosphere, so they become relevant at the global scale. These include GHGs, which accumulate in the troposphere, alter the radiation balance and contribute to global-scale climate changes. These include increases in tropospheric temperatures, changes in precipitation patterns, reduction in sea ice extent and the rise of global sea level (IPCC, 2013). The contribution of cities to global GHG emissions and the consequences of global climate changes on cities are discussed in Chapter 13.

**Summary**

Good air quality is a very valuable asset, but maintaining it is a challenge for cities where people are proximate to multiple sources of air pollutant emissions, often in confined spaces like buildings or street canyons. In general terms, air quality is controlled by the strength and density of emission sources, the ability of the atmosphere to mix and advect air pollutants and the chemical and physical transformation and removal of air pollutants. These controls are specific to individual cities and the climates they occupy.

- The intensity of emissions and the suite of air pollutants in the urban atmosphere depend mainly on the nature of the local economy, the energy base that underpins it, and the technology used. The first determines the relative contributions and intensity of emissions from residential, commercial, industrial and transportation sectors, while the type of fuel (coal, oil, gas, etc.) controls the character of the emissions. Emission control technology, if present, can help prevent or remove unwanted combustion products.
- The form and design of the city in conjunction with its economic functions determines the geography of emissions. Air pollutants emitted within buildings, or within the urban canopy layer (UCL), can become highly concentrated if ventilation is weak. Exchanges across the top of the UCL, in addition to emissions above this level, contribute to air quality in the urban...
boundary layer (UBL) where they can cause chemical reactions that create secondary pollutants, sometimes at considerable distances downwind from major urban emission areas.

- **Wind, turbulence and stability** play a critical role in determining the mixing and dispersion of air pollutants at all scales in the city. At the microscale the pattern of wind within the UCL is managed by urban form that helps circulate and channel air pollutants. Within the UBL, wind and the mixed layer height regulate the volume of atmosphere into which air pollutants are mixed. Aspects of the urban climate such as the urban heat island can modify these climate controls.

The focus of air quality management is mainly to regulate emissions, although ensuring their mixing and dilution through design, is an ancillary option. Regulation can be achieved indirectly through urban planning and design (see Chapter 15) and directly though ‘command-and-control’ legislation. Decisions taken to improve air quality must account for the full life cycle of air pollutants in a broader geographic setting, including areas downwind of the city (see Chapter 12).