

# 1

## Introduction to Air Pollution

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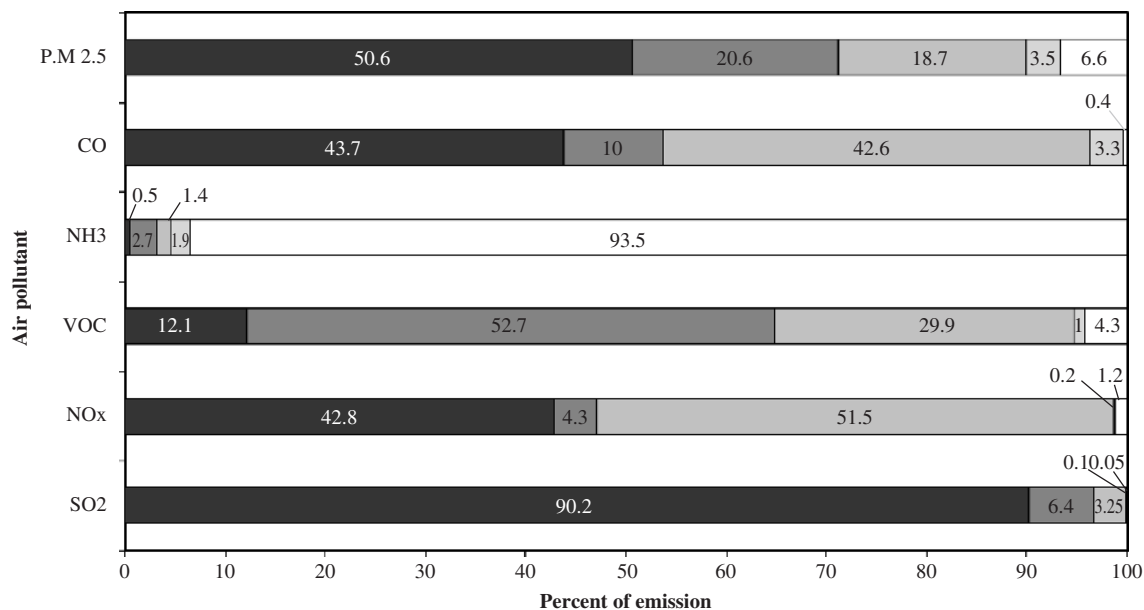
### 1.1 Introduction

This book describes the different biodegradation processes and bioreactors available for air pollution control as well as other alternatives for reducing air pollution, mainly by using more environmentally friendly fuels and biofuels, such as ethanol, hydrogen, methane or biodiesel. Only the bioreactors and (bio)fuels most widely used or studied over the past decade are reviewed in this book. Bioreactors, for which not much significant research or many new developments have occurred over the past decade, have been described in other book chapters [1] and are not included in this book.

### 1.2 Types and sources of air pollutants

Two major groups of pollutants can be considered in terms of air pollution: particulate matter and gaseous pollutants. The latter may be subdivided into volatile organic compounds (VOCs) and volatile inorganic compounds (VICs). The best available treatment technology will depend on the composition and other characteristics of the emissions to be treated. The most significant contaminants and their origin are shown in Figure 1.1, in terms of emission percentages, in 2006 by source category for the 27 member states of the European Union. The member states are (year of entry in brackets) Austria (1995), Belgium (1952), Bulgaria (2007), Cyprus (2004), Czech Republic (2004), Denmark (1973), Estonia (2004), Finland (1995), France (1952), Germany (1952), Greece (1981), Hungary (2004), Ireland (1973), Italy (1952), Latvia (2004), Lithuania (2004), Luxembourg (1952), Malta (2004), The Netherlands (1952), Poland (2004), Portugal (1986), Romania (2007), Slovakia (2004), Slovenia (2004), Spain (1986), Sweden (1995) and the United Kingdom (1973).

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From left to right:

- Stationary sources: Combustion processes
- Stationary sources: Industrial, non combustion processes
- Mobile sources: Road and nonroad origin
- Waste disposal
- Miscellaneous (including agriculture)

**Figure 1.1** Distribution of EU-27 total emission estimates for different pollutants, by source category, in 2006.

Table 1.1 and Table 1.2 compare the annual emission estimates for both the European Union (EU-27) and the United States, considering anthropogenic land-based sources only [2]. Natural sources of emission and other possible sources such as navigation have not been included, as comparable information for Europe (EU-27) and the United States often could not be obtained. Although some recent data were sometimes not available for the United States and needed to be extrapolated [2], it is still possible and accurate to conclude that the results follow in both cases a similar trend for the different pollutants, in terms of both the relative total emission of each pollutant and the source of pollution. However, some differences may still be found when analysing the tables in detail, mainly in the case of carbon monoxide (CO) emission. For example, in Europe, almost 43% of CO emissions come from mobile sources (vehicles and transportation in general), while this represents as much as 85% in the United States. Conversely, CO from combustion sources represents about 44% in Europe, while it is only 7% in the United States.

**Table 1.1** 2006 emission estimates for different pollutants, by source category, in the European Union (EU-27) ( $10^6 \text{ kg yr}^{-1}$ ). Reprinted under the terms of the STM agreement from [2] Copyright (2012) Elsevier Ltd.

Category	CO	NH <sub>3</sub>	VOC	NO <sub>x</sub>	PM <sub>2.5</sub>	SO <sub>2</sub>
Stationary sources: combustion	22 979	33	1 831	7 175	1 619	13 868
Stationary sources:noncombustion	5 254	167	7 954	721	660	980
Mobile sources	22 421	86	4 511	8 642	598	501
Waste treatment and disposal	1 726	121	148	36	114	14
Miscellaneous (mainly agriculture)	224	5 885	657	197	211	8
Total	52 604	6 292	15 101	16 771	3 202	15 371
% of total	48.1	5.8	13.8	15.3	2.9	14.1

**Table 1.2** 2006 emission estimates for different pollutants, by source category, in United States ( $10^6 \text{ kg yr}^{-1}$ ). Reprinted under the terms of the STM agreement from [2] Copyright (2012) Elsevier Ltd.

Category	CO	NH <sub>3</sub>	VOC	NO <sub>x</sub>	PM <sub>2.5</sub>	SO <sub>2</sub>
Stationary sources: combustion	5 619	63	843	6 206	1 150	12 026
Stationary sources:noncombustion	3 009	205	7 960	1 724	758	2 708
Mobile sources	69 735	291	6 913	10 810	962	499
Waste treatment and disposal	1 416	25	375	131	241	27
Miscellaneous (mainly agriculture)	1 949	3 679	495	61	561	20
Total	81 728	4 263	16 586	18 932	3 672	15 280
% of total	58.2	3.0	11.8	13.5	2.6	10.9

### 1.2.1 Particulate matter

Particulate matter can be defined as a small solid or liquid mass in suspension in the atmosphere. Primary particles are directly emitted from a polluting source, while secondary particles are formed in the atmosphere as a result of reactions or interactions between pollutants and/or compounds present in the atmosphere, usually volatile organic compounds, nitrogen oxides or sulphur oxides as well as water. A water droplet of acid rain, carrying sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) or nitric acid (HNO<sub>3</sub>) produced from nitrogen oxides (NO<sub>x</sub>) or sulphur oxides (SO<sub>x</sub>), would be classified as particulate matter. Different terms can be used for particles (e.g. dust, smoke, mist or aerosol) depending on their nature and characteristics.

Although many particles are not spherical, for the sake of simplicity and for engineering calculations, nonspherical particles are often assimilated to spheres of the same volume as the original particle. *Particle size*, then, refers to the corresponding particle diameter.

Typically, the size (diameter) of particulate matter found in polluted air or waste gases may vary between about  $10^{-2} \mu\text{m}$  and a few hundreds of micrometres ( $10^{+2} \mu\text{m}$ ), although smaller and larger particles may also be found. Larger particles do, however, settle quite fast, and in that way are quickly eliminated from the atmosphere. In order to give an idea of the scale,  $10^{-2} \mu\text{m}$  is a common size for viruses, while coal particles, flour or cement dust may be around  $10^{+2} \mu\text{m}$ . The sizes of the latter may, however, vary

considerably, between only a few micrometres and about 1 mm. The same is true for water droplets, for example mist or raindrops, with sizes ranging between a few micrometres up to more than 1 mm. Particles of 10  $\mu\text{m}$  are considered large particles. Particulate matter is classified as  $\text{PM}_{10}$  for sizes up to 10  $\mu\text{m}$ , and  $\text{PM}_{2.5}$  for smaller sizes up to 2.5  $\mu\text{m}$ .

The effect of particles on health is more important in the case of smaller particles, for instance those below 2.5  $\mu\text{m}$ , as they will more easily reach the lungs than larger particles. Some particles may carry heavy metals and carcinogenic molecules. They can also cause disorders of the respiratory system, asthma, bronchitis and even heart problems. Besides, particles can reduce visibility and be involved in acid precipitations, or *acid rain*, described later in this chapter.

### 1.2.2 Carbon monoxide and carbon dioxide

According to data of the European Environment Agency and the US Environmental Protection Agency (EPA), the highest emission of gaseous pollutants to the atmosphere corresponds to emissions of CO, in both the European Union and the United States (Table 1.1 and Table 1.2). Close to 50%, or somewhat more, of the total anthropogenic emission of pollutants corresponds to CO. Large amounts may be produced by natural sources as well. On average, mobile sources account for about 85% of the total CO emissions in the United States. It reaches 42.6% in Europe; another 43.7% come from combustion processes in stationary sources (Figure 1.1). Considering that a large part of mobile sources are vehicles such as cars and trucks, it becomes obvious that CO pollution will be more significant in urban areas. As mentioned, the second largest source of CO emission, after motor vehicle exhaust, corresponds to stationary combustion processes and other industrial production processes. Its main origin is the incomplete combustion of fossil fuels or other materials such as wood. Combustion is the result of a reaction between oxygen and a fuel. Carbon dioxide, water and heat will be produced if the reaction is complete and if the fuel contains only carbon, hydrogen and, eventually, oxygen atoms, such as in the example of methane (a major chemical present in natural gas):



Carbon monoxide, instead of carbon dioxide, will be formed when the combustion is not complete, as shown in this reaction:



Several reasons may be involved in this incomplete reaction. The most important ones are the amount of available oxygen, temperature, reaction time and turbulence. The theoretical amount of oxygen needed for complete combustion can be calculated from the stoichiometric equation. However, some excess air is generally recommended for ensuring complete oxidation, but not too much, since excess air needs to be heated as well. Increasing the temperature and residence time in the combustor will be favourable to complete combustion, as well as increasing turbulence in order to achieve intimate mixing between the oxygen and fuel.

Carbon monoxide is not of significant concern in terms of its impact on the environment, but it is flammable and, above all, highly toxic when inhaled. It is an odourless and colourless gas. Therefore, its presence is difficult to detect in closed environments. Prolonged exposure to concentrations above 50–100 ppmv will cause fatigue, nausea and headache, while several hours of exposure to concentrations exceeding 400–500 ppmv will gradually lead to dizziness and death. Carbon monoxide combines with haemoglobin (Hb) in the blood and in that way prevents haemoglobin from transporting oxygen from the respiratory organs to the tissues. The affinity between CO and Hb is much stronger than that between Hb and oxygen.

Similarly to CO, the major source of carbon dioxide (CO<sub>2</sub>) is combustion. It is only recently that CO<sub>2</sub> has been considered a compound of environmental concern. Pollutants such as CO<sub>2</sub>, methane and nitrogen oxides are all greenhouse gases, supposed to play a key role in global temperature changes. The average residence time of CO<sub>2</sub> at concentrations typically found in the atmosphere is about 15 years, while it is about 10 weeks for the much more reactive CO molecule. The concept of residence time of a species in the atmosphere is similar to the residence time of a molecule in a continuous reactor. It is the average time that species spends in the atmosphere before disappearing, for example through chemical or photochemical reactions. Such difference in residence time between CO and CO<sub>2</sub> justifies the negligible increase of the CO concentration in the air over the past century compared to CO<sub>2</sub>. Actually, one major product formed from atmospheric CO is CO<sub>2</sub>. The normal concentration of CO<sub>2</sub> in nonpolluted air currently is around 380 ppmv, whereas it hardly reached 300 ppmv a century ago.

### 1.2.3 Sulphur oxides

Sulphur oxides (SO<sub>x</sub>) include both sulphur dioxide (SO<sub>2</sub>) and sulphur trioxide (SO<sub>3</sub>). Sulphur dioxide appears in larger amounts than SO<sub>3</sub> in combustion gases and is largely released during the combustion of fossil fuels, mainly coal, in stationary sources, according to the following equations:



As shown in Figure 1.1, stationary combustion processes represent by far the major source of SO<sub>2</sub>, with around either 80% or 90% of the total SO<sub>x</sub> emissions, respectively, in the United States and EU-27. The average residence time of SO<sub>2</sub> in the atmosphere is about 5–6 weeks. That pollutant is largely generated at electric power plants. Its concentration in combustion gases will depend on the amount of sulphur present in the original fuel, which usually does not exceed 3–4% by weight but may occasionally reach 10%. Oil does, in most cases, contain higher amounts of sulphur than coal, while sulphur content is basically negligible in natural gas. Part of that sulphur may be removed from the fuel to reduce emissions during combustion.

In terms of environmental impact, SO<sub>2</sub> can react with moisture in the air to form H<sub>2</sub>SO<sub>4</sub>, leading to acid precipitation commonly known as *acid rain*. In terms of health effects, SO<sub>2</sub> can cause respiratory disorder and lung diseases.

A small amount of the SO<sub>2</sub> formed during combustion may be further oxidized to SO<sub>3</sub>, usually not more than 5%. Its concentration will increase at higher temperature and in the presence of excess oxygen. SO<sub>3</sub> has a much higher corrosion potential than SO<sub>2</sub>. It is important to prevent its condensation in the plants. Sulphur trioxide may react with water vapour to produce H<sub>2</sub>SO<sub>4</sub>. Besides, SO<sub>3</sub> has been reported to be 10 times more toxic than SO<sub>2</sub>, mainly for the respiratory system [3].

### 1.2.4 Nitrogen oxides

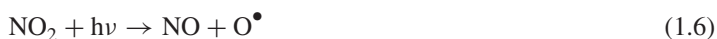
Among the different oxides of nitrogen (nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), nitrate (NO<sub>3</sub>), nitrous oxide (N<sub>2</sub>O), dinitrogen trioxide (N<sub>2</sub>O<sub>3</sub>), dinitrogen tetroxide (N<sub>2</sub>O<sub>4</sub>) and dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>)), the symbol NO<sub>x</sub> refers to the sum of NO and NO<sub>2</sub> which are considered to be the major relevant contaminants of that group in the atmosphere. NO and NO<sub>2</sub> have average residence times in the air close to one day. Other oxides of nitrogen generally appear only at very low concentrations in NO<sub>x</sub>-polluted environments. On reaction with atmospheric moisture, NO<sub>x</sub> form small particles. The environmental impact of N<sub>2</sub>O has also been discussed, although, for historical reasons, that compound is not included in the group of NO<sub>x</sub> as

such. N<sub>2</sub>O is a major greenhouse gas, similarly to methane and CO<sub>2</sub>, but with a global warming potential almost 300 times higher than that of CO<sub>2</sub>. The *global warming potential* of a pollutant is an estimation of its ability to trap heat or infrared radiation reflected by the Earth's surface. Agriculture is a major source of anthropogenic N<sub>2</sub>O emissions to the atmosphere, through nitrification of ammonium-containing fertilizers and animal waste or denitrification of NO<sub>3</sub> in soils. Contrary to NO<sub>x</sub>, N<sub>2</sub>O is not directly a product of fuel combustion.

NO<sub>x</sub> react with hydrocarbons and oxygen in the presence of ultraviolet (UV) radiation to produce photochemical smog, mainly in urban areas. They can cause eye and skin irritation and have adverse effects on the respiratory system and on plants. In the atmosphere, NO generated during combustion will eventually be converted to NO<sub>2</sub>. Besides, NO<sub>2</sub> reacts with the hydroxyl radical from water to form HNO<sub>3</sub>. It is then eliminated from the atmosphere by either dry deposition or wet deposition, resulting in the latter case in *acid rain*, as summarized in the following reactions:

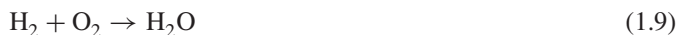


As shown in the reactions in Equations (1.6), (1.7) and (1.8), NO<sub>2</sub> leads to the formation of unwanted ground-level ozone, in the presence of UV light and volatile organic compounds, in the lower atmosphere. The reactions are temperature dependent, and more ozone is detected in the air at higher temperature (i.e. during the day and in the summer period).



Part of the ozone formed from NO<sub>2</sub> is removed through a reaction of O<sub>3</sub> with NO. This suggests that other mechanisms or compounds must be involved in ozone accumulation in the atmosphere. It will be shown, in Section 1.2.5, that VOCs also play a key role in the overall process.

As much as about 90% of NO<sub>x</sub> are emitted into the atmosphere during combustion processes, from either mobile sources or stationary sources. Nitrogen oxides are formed from both nitrogen naturally present in combustion air (in which case it is called *thermal NO<sub>x</sub>*) and nitrogen compounds found in the fuels. The reaction between nitrogen and oxygen is significant only at high temperatures. The influence of temperature on the rate of NO<sub>x</sub> formation is, however, highly variable and depends on the source of nitrogen. Its formation may also sometimes depend on the involvement of hydrocarbons in the reaction. Depending on its origin, fuel oil generally does not contain more than 0.5% nitrogen by weight. Conversely, coal may contain up to 2–3% nitrogen by weight, where it is mainly combined with carbon in the form of polycyclic aromatic rings. Those C—N bonds are more stable than C—C bonds and need high temperatures to be converted to NO<sub>x</sub>. It was mentioned in this chapter that natural gas contains hardly any sulphur. The same is true for nitrogen. Natural gas is thus a quite clean fuel in terms of NO<sub>x</sub> and SO<sub>x</sub> emissions. Besides, natural gas emits virtually no particulate matter compared to coal and oil. The products of its combustion are mainly water vapour and CO<sub>2</sub>, if complete oxidation takes place. It is estimated that the world would run out of coal in about 200–300 years based on current consumption estimations, while the sources of oil and natural gas would presumably get exhausted before the end of this century. It is worth mentioning that the use of hydrogen as a source of energy would theoretically not produce any NO<sub>x</sub>, according to the following reaction:



However, this is generally not totally true in practice. In the presence of air, hydrogen may even produce more NO<sub>x</sub> than during natural gas combustion, as a result of the reaction involving nitrogen and oxygen naturally present in air.

Ammonia ( $\text{NH}_3$ ) is another important nitrogen-bearing pollutant (see also Chapter 2). In most developed countries, more than 80% of  $\text{NH}_3$  emission originates from agricultural activities, mainly livestock and poultry operations on the one hand and the use of fertilizers on the other. Farm animals used to produce milk, meat or eggs are often fed food with high protein content. A nonnegligible fraction of it is not metabolized and is excreted in the urine and faeces, which represent the main components of manure. Ammonia is released during the microbial decomposition of manure. The other major source of ammonia emission is through the use of mineral fertilizers. Only about 50% of the nitrogen (mainly urea) present in high-nitrogen fertilizers is taken up by crops and forage species. A large part of the nitrogen is lost mainly through gaseous emissions, but also through leaching, erosion or runoff.

### 1.2.5 Volatile organic compounds (VOCs)

There are different definitions of VOCs, but most of them generally agree on some specific aspects. VOCs are *organic* compounds or, in other words, carbon-containing molecules that also contain other species, such as H or O. It is worth recalling that hydrocarbons and VOCs are not the same. Some hydrocarbons are indeed VOCs, composed of only C and H atoms, but not all VOCs are hydrocarbons. Some organic molecules have traditionally been excluded from this definition used in organic chemistry and are not included in the list of VOCs, such as carbon monoxide, carbon dioxide, carbonates, carbides and cyanides, which are classified as inorganic compounds. VOCs are *volatile*. The vapour pressure at room temperature or, otherwise but less frequently, the boiling point at atmospheric pressure is often considered to decide whether a compound is volatile or not. According to the European EC-Directive 1999/13/EC, VOCs have a vapour pressure of  $10^{-2}$  kPa or more at 293.15 K (20 °C). VOCs are molecules with a boiling temperature usually below about 240–250 °C at 101 325 Pa (normal atmospheric pressure). However, the border between *volatile* and *nonvolatile* organic compounds is somewhat arbitrary. Additionally, some definitions add that VOCs should participate in *photochemical reactions* in the atmosphere. However, not all VOCs, as defined here based on their vapour pressure or boiling point, exhibit significant photochemical reactivity. As shown in Figure 1.1, the major sources of VOCs are industries, which represent about 50% of the overall emission estimates. VOCs may exert highly different and variable effects on human health. Depending on their nature, they may irritate the eyes, nose and throat, or act as central nervous system depressants. Some VOCs are carcinogenic. They are also frequently found in indoor air, as they are present in most paints, varnishes, waxes, glues, cleansers and cosmetics, among others. In terms of environmental impact, VOCs play a key role in the formation of ozone in the lower atmosphere.

It was shown in Section 1.2.4 (Equation (1.8)) that part of the ozone formed in the troposphere is later destroyed through a reaction with nitric oxide.



However, NO will also react with VOC in the air. This will reduce the amount of available NO that could potentially react with ozone. The latter will then accumulate in the atmosphere. Although the overall process is quite complex and involves several reactions, the effect of VOC (here:  $\text{ROO}^\bullet$ ) on NO removal can be summarized in the following reaction



It is interesting to observe both the elimination of NO in that reaction and the formation of  $\text{NO}_2$ , which is one of the precursors of ozone formation.

Among the many different VOCs, methane ( $\text{CH}_4$ ) is known for its impact on global warming, with a global-warming potential 25 times higher than that of  $\text{CO}_2$ . This means that its impact on temperature

**Table 1.3** Common groups and examples of VOC pollutants.

Group of VOCs	Examples
<i>Pollutants containing only C, H and/or O</i>	
Alkanes	Methane, butane, hexane
Alkenes	Acetylene, ethylene
Ketones	Acetone, methylethyl ketone (MEK) Methyl iso butyl ketone (MIBK)
Aldehydes	Formaldehyde, acetaldehyde, benzaldehyde
Alcohols	Methanol, ethanol, propanol
Acids	Acetic acid, butyric acid, formic acid
Aromatic compounds (usually monocyclic)	Benzene, toluene, xylenes, ethylbenzene, styrene, $\alpha$ -pinene
<i>Pollutants including species other than C, H and/or O</i>	
Halogenated alkanes	Chloromethanes
Halogenated alkenes	Tetrachloroethylene (PCE), trichloroethylene (TCE), vinyl chloride
Halogenated aromatic compounds (monocyclic)	Chlorobenzenes
Sulphur compounds	Carbon disulphide, (di)methyl (di)sulphide, ethanethiol
Nitrogen compounds	Trimethyl amine

over a 100-year period will be 25 times that of the same amount of CO<sub>2</sub>. Some of the main sources of methane are agriculture, ruminants, wetlands and landfills. The typical concentration of methane in clean air is currently around 1800 ppb. Methane is sometimes excluded from the list of VOCs. Those pollutants are then divided into methane VOCs as a specific pollutant and nonmethane volatile organic compounds (NMVOCs). Other examples of VOCs are listed in Table 1.3. This is not an exhaustive list, since a very wide range of different VOCs is known.

### 1.2.6 Odours

In the case of air pollution, the word *odour* refers to the ability of a pollutant or mixture of pollutants to activate the sense of smell. Odour nuisance is generally the result of a nasty smell. A pleasant odour may become nasty at high concentrations or after long-term exposure. Both organic and inorganic compounds may lead to odour nuisance. Two common examples are hydrogen sulphide (H<sub>2</sub>S, a VIC) and butyric acid (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>—COOH, a VOC). Hydrogen sulphide smells like rotten eggs. Its odour threshold value is 0.014 mg m<sup>-3</sup>. Butyric acid has a sweet rancid odour and an odour threshold of about 0.001 mg m<sup>-3</sup>.

The intensity of odour nuisance is expressed in terms of odour units per cubic metre [1]. The European odour unit is the amount of pollutant that, when diluted in 1 m<sup>3</sup> of an inert gas (generally pure air) under standard conditions, leads to the same physiological response from a panel (detection threshold) as a European reference odour mass (EROM) in 1 m<sup>3</sup> gas. One EROM is equivalent to 123  $\mu$ g *n*-butanol m<sup>-3</sup> neutral gas.



### 1.2.7 Ozone

Ozone formation in the lower atmosphere, called the *troposphere* (i.e. between ground level and about 10–12 km), is known as a secondary contaminant. Secondary contaminants are pollutants formed from a reaction between other compounds in the atmosphere; this is contrary to primary contaminants, as described in the previous sections of this chapter, which are directly released from emission sources. As mentioned, ground-level ozone has adverse effects on human health and the environment. It may cause asthma and other respiratory problems. It plays a key role in photochemical smog, and it damages plants and agricultural crops. Conversely, ozone in the upper atmosphere (stratosphere) is desirable as it helps to filter UV radiation. Exposure to excess UV light is considered to cause skin cancer and other related problems.

### 1.2.8 Calculating concentrations of gaseous pollutants

The concentration of a given VOC or VIC in polluted air or waste gases is often expressed in  $\text{mg m}^{-3}$ . Those units can be converted to ppb or ppmv (sometimes simply called *ppm*). The abbreviation *ppb* means parts per billion. In the case of volatile pollutants present in the gas phase, 1 ppb corresponds to one volume of pollutant diluted in  $10^9$  volumes of gas, that is, pollutant + air (or waste gas). Similarly, 1 ppmv will be 1 volume of pollutant diluted in  $10^6$  volumes of gas.

Concentrations expressed in  $\text{mg m}^{-3}$  can easily be converted to ppmv and vice versa. Under normal conditions of pressure and temperature (101 325 Pa, 273 K):

$$1 \text{ mg m}^{-3} = (22.4/\text{MW}) \text{ ppmv}$$

where MW stands for the molecular weight of the pollutant and 22.4 is the molar volume of the pollutant at such pressure and temperature. At 298 K (25 °C), the molar volume would be 24.5 instead of 22.4 [1].

In other words, in order to convert the concentration of, for example,  $1 \text{ mg m}^{-3}$  methane to ppmv, at 273 K and 1 atm, one should do the following calculation:

$$1 \text{ mg}_{(\text{CH}_4)} \text{m}^{-3} = (22.4/16.04) \text{ ppmv}_{(\text{CH}_4)} = 1.42 \text{ ppmv}_{(\text{CH}_4)}$$

Thus,  $1 \text{ mg}_{(\text{CH}_4)} \text{m}^{-3}$  and  $1.42 \text{ ppmv}_{(\text{CH}_4)}$  are the same.

## 1.3 Air pollution control technologies

### 1.3.1 Particulate matter

Bioreactors are not suitable for the removal of particulate matter from waste gases. The only biological alternative suitable to efficiently reduce the amount of particulate matter emitted into the atmosphere would be the use of more environmentally friendly fuels or biofuels generating less particles upon combustion. Whenever the effluent contains both volatile pollutants and particles, the latter will need to be eliminated first if one plans to remove the volatile pollutants in a bioreactor, above all in the case of using packed-bed bioreactors. Otherwise, particles would end up clogging the packed bed.

The five most common groups of processes used for the removal of particles from waste gases are gravity settling, cyclone collection, filtration, electrostatic precipitation and absorption [1]. Some information on their principles and basic characteristics are summarized in Table 1.4. More detailed information can be found in specialized literature.

**Table 1.4** Characteristics of technologies suitable for the removal of particulate matter.

	Gravity settling chamber	Cyclone	Filter bags	Electrostatic precipitators	Scrubbers
Removal principle	Settling as a result of gravitational forces	Centrifugal force	Physical barrier (fabric filter) retaining particles and letting the gas (air) pass through	Electric force – charging the particles migrating from the gas to a collecting plate of opposite polarity	Gas–liquid mass transfer + increase of particle–droplet size
Typical diameter of particles removed (> 90%)*	>50–100 $\mu\text{m}$	>10 $\mu\text{m}$	>0.5–2 $\mu\text{m}$	>0.1 $\mu\text{m}$	>1 $\mu\text{m}$
Treatable gas velocities	Low	Average	Average–high	High	Average–high
Cost	Low	Low	High (mainly the bags themselves)	High	Medium

\*Indicative only; highly dependent on the characteristics of the waste gas and operating conditions.

## 1.3.2 Volatile organic and inorganic compounds

### 1.3.2.1 Nonbiological processes

Methods used for the removal of volatile pollutants are based on either mass transfer or chemical or biological reactions. In the case of mass transfer, the pollutant is transferred from one phase (gas) to another phase. This is the case in absorption and adsorption processes. It means that such technologies may sometimes allow for the recovery of the pollutant, if needed. This is important and useful if the pollutant, for example an organic solvent, is expensive and/or if it needs to be reused. Conversely, if it does not need to be recovered, its transfer from the gas phase to another phase (e.g. liquid or solid) will generally lead to the contamination of that new phase. It will be necessary to treat or dispose of that new, polluted phase. Methods based on some kind of reaction transform the pollutant into other products, which are usually innocuous if the process has been optimized. This is the case for bioreactors and nonbiological oxidation processes. Bioreactors are used for the biodegradation or bioconversion of pollutants, while incineration relies on nonbiological reactions of oxidation.

**Absorption** In waste-gas treatment, absorption is a gas–liquid mass transfer process and may be used for the removal of both particulate matter and volatile pollutants. The most common absorption columns are spray chambers, sieve trays or plate columns and packed-bed columns; the latter are the most popular configuration for waste-gas treatment. The fluids (gas and liquid) may flow through the column co-currently, counter-currently or in a cross-flow mode. In the first case, both fluids enter through the top of the tower. In counter-current operation, which is the most common design, the liquid is introduced at the top and the gas at the bottom of the column. In cross-flow, the gas follows a horizontal path through the absorption

column, while the liquid flows vertically through the packed bed, as a result of the effect of gravity. Absorption may be due to mass transfer only or it may, simultaneously, involve a chemical reaction. The main interest of a chemical reaction is to increase the solubility of the compound to be absorbed in the liquid phase, thus improving the efficiency of the process. Several factors will affect the rate and efficiency of pollutants removal. The mass transfer rate is directly related to the difference between the concentration of the pollutant in the gas phase and in the liquid phase, also called the *driving force*, and expressed as follows:

$$N_{\text{Pollutant}} = K_Y (y_P - y_P^*), \quad (1.11)$$

where  $N_{\text{Pollutant}}$  is the transfer rate of pollutant P (kmoles  $\text{m}^{-2} \text{h}^{-1}$ ),  $K_Y$  is the overall gas mass transfer coefficient and  $(y_P - y_P^*)$  is the driving force with  $y_P$  being the gas mole fraction of P in the bulk gas phase and  $y_P^*$  being the gas mole fraction of P that would be in equilibrium with  $x_P$  (i.e. the mole fraction of P in the bulk liquid phase) (Figure 1.2).

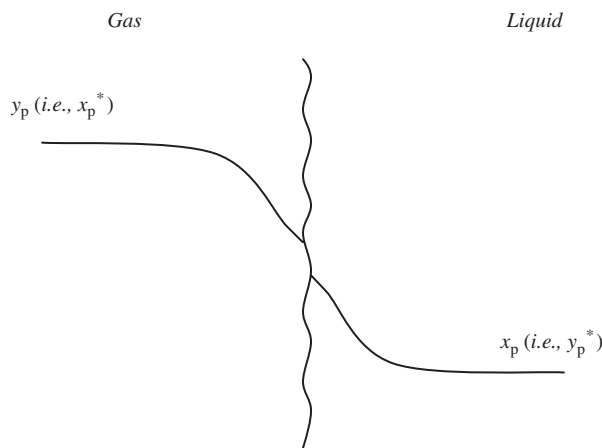
A similar equation can be written in terms of the overall liquid mass transfer coefficient,  $K_X$ , yielding the same  $N_{\text{Pollutant}}$  value:

$$N_{\text{Pollutant}} = K_X (x_P^* - x_P), \quad (1.12)$$

where  $(x_P^* - x_P)$  is the driving force with  $x_P$  being the liquid mole fraction of P in the bulk liquid phase and  $x_P^*$  being the liquid mole fraction of P that would be in equilibrium with  $y_P$  (i.e. the mole fraction of P in the bulk gas phase).

In air pollution, the concentration of pollutant in the gas phase is generally low. Under such conditions, the equilibrium relationship between the pollutant concentration in the gas phase and in the liquid phase is generally linear.

Some key parameters to be chosen that allow optimization of the process are the packing and the nature and hydrodynamic characteristics of the liquid. Whenever possible, water will be used as the liquid phase, as it is cheap and readily available in large quantities. It presents several other advantages: it is inert, nontoxic and noncorrosive and has a low volatility. The liquid flow rate should be optimized and depends, among others, on the packing and on the gas flow rate. The process should be designed in such a way that it avoids reaching *flooding conditions*. The latter corresponds to a situation where the gas velocity will hold up the liquid in such a way that it will no longer be able to flow through the column. Too high liquid



**Figure 1.2** Transfer of a pollutant from a gas phase to a liquid phase (two-liquid-film theory).

flow rates will lead to high pressure drops and may also result in flooding conditions, as it may be difficult for such high volumes of liquid to flow through the column. A homogeneous gas and liquid distribution of both fluids through the column is of prime importance to work under optimal conditions. For high towers, it may be necessary to collect and redistribute the liquid at a given packing height, depending on the packing characteristics.

The packing is another key parameter in absorption towers. Packings can be divided into two groups: on the one hand structured packings and on the other packings introduced randomly in the column. The most common materials are plastic, ceramic and stainless steel. Some important characteristics of packings are the specific surface area and the void space. A higher surface area will improve mass transfer. A higher void space will minimize pressure drop, as the fluids will have more space to flow freely through the column.

**Adsorption** Adsorption is a fluid–solid mass transfer technology, in which the pollutant to be adsorbed is called the *adsorbate* and the adsorbing solid is called the *adsorbent*. The fluid is a gas in the case of gas treatment. The adsorbate adheres to the solid surface either through physical adsorption or through chemisorption. In physical adsorption, weak physical bonding forces are created, mainly van der Waals forces, while stronger chemical bonds are formed in chemisorption. The most common adsorbent, in air or gas pollution control, is activated carbon (AC). It is used in the form of pellets or granules of sizes generally ranging from less than 1 mm to a few millimetres. AC is quite efficient for the removal of many VOCs, though not all pollutants will be retained with the same efficiency. Inorganic compounds such as H<sub>2</sub>S are also well adsorbed onto AC. The latter is produced through a heat treatment of carbonaceous materials (e.g. coal, wood, shells and peat) in the absence of oxygen followed by steam treatment, resulting in a solid with a very high surface area, often close to about 1000 m<sup>2</sup> g<sup>-1</sup>. The adsorbent is usually introduced in a fixed-bed column. The contaminated gas phase flows through the bed and the pollutants are retained inside the bed, while clean gas is released to the atmosphere.

Spent AC can be regenerated and reused, once it is exhausted and its surface is saturated with pollutants or other adsorbates. This avoids costly disposal. Carbon regeneration is generally done through thermal reactivation with steam, at temperatures in the range of 100–140 °C. Desorbed gases can be recovered and reused.

The equilibrium relationship is expressed mathematically by means of *adsorption isotherms*, representing the amount of adsorbate adsorbed on the solid material versus its concentration – or equilibrium partial pressure (atm) – in the gas phase. Different mathematical equations can accurately represent the equilibrium data, at a given temperature, depending on parameters such as the type of pollutant or the adsorbent. The equilibrium relationship is generally not linear. The most common equilibrium equations are the Langmuir isotherm, Freundlich isotherm and Brunauer–Emmett–Teller (BET) equation.

**Thermal and catalytic oxidation** In oxidizers, volatile pollutants react with oxygen at high temperature – as a result of the combustion of a fuel – to form, mainly, CO<sub>2</sub> and water, if complete degradation takes place. It is worth mentioning that fuel combustion contributes to the release of high amounts of CO<sub>2</sub>, besides the amount of CO<sub>2</sub> released from the oxidation of the volatile pollutants themselves. Almost any type of natural gas can be considered as suitable fuel. Other products, such as acids, may also be formed when halogenated pollutants are present in the waste gas. Hydrogen chloride in oxidizers treating chlorinated compounds needs to be removed and may be eliminated, for example, in a scrubber. Free chlorine is sometimes also released during such oxidation process. SO<sub>2</sub> will be produced when sulphur-containing VOCs are oxidized. NO<sub>x</sub> may also appear in the combustion gases, if the pollutants contain N or as a result of the oxidation of nitrogen present in the air used for combustion, above all at high temperatures.

Besides the amount of available oxygen, three other key factors allow optimization of the oxidation process, namely, temperature, time and turbulence.

The minimum amount of oxygen (air) needed for complete oxidation to take place can be calculated from the stoichiometric equation of the oxidation reaction. A lack of oxygen will produce some CO instead of CO<sub>2</sub> as a combustion product. Therefore, some oxygen in excess is recommended. However, too much excess oxygen should be avoided, as excess air will take away part of the heat needed for the oxidation of the waste gas.

Either thermal oxidizers or catalytic oxidizers may be used. In thermal oxidation, operating temperatures are commonly in the range of 700–1000 °C. Higher temperatures, exceeding 1000 °C, may be needed for specific applications or if high destruction efficiencies (usually > 99%) must be reached. In catalytic oxidation, the flue gas is preheated and then exposed to a catalyst. The presence of a catalyst increases the reaction rate and allows catalytic oxidizers to be operated at lower temperatures, typically around 300–500 °C. Thus, they require substantially less fuel, reducing in that respect the operation costs. However, the need for costly catalysts will increase the investment costs. Nevertheless, lower temperatures can be applied, resulting in reduced construction costs, which contribute to the investment costs as well. The catalyst contains either noble metals, such as platinum or palladium, or metal oxides. It often undergoes gradual deterioration and needs to be regenerated or replaced after 2–5 years.

Residence times typically applied in thermal and catalytic oxidizers are in the range of 0.1–2.0 seconds. Similarly as for temperature, a higher residence time should improve the destruction efficiency. Thus, either temperature or residence time – or both – may be increased in order to improve the removal of pollutants. A higher temperature will increase the operation costs, while the investment costs will be more if a longer residence time (i.e. larger oxidizer volumes) needs to be applied.

Good mixing will improve the efficiency of the oxidation process. A high turbulence will optimize the reaction between the fuel and oxygen from air (i.e. the fuel combustion). It will also ensure good mixing between the fuel combustion gas and the waste gas that will better reach its combustion temperature. Introducing baffles in the oxidizer helps create a higher turbulence, although it may also result in the presence of unwanted dead zones.

### **1.3.2.2 Bioprocesses**

Most of the bioprocesses and bioreactors suitable for air pollution prevention and control are described further in this book, focusing on both biodegradation and bioconversion technologies. One of the oldest bioprocesses, developed in the mid-20th century, for waste-gas treatment is the conventional open biofilter, which is used mainly to solve odour problems at wastewater treatment plants and composting facilities (Chapter 4) [4]. Sulphur compounds, such as H<sub>2</sub>S, are typical odorous pollutants in such waste gases, and their biological removal has been extensively studied and optimized in full-scale processes. Gas-loading rates treated originally in such conventional biofilters were quite low. In the 1980s, significant research and improvements were made. Later, closed biofilters were developed as well as biotrickling filters (Chapter 5). Laboratory-scale studies were then performed that studied the potential removal of VOCs typically found in industrial waste gases from process industries. However, applied research and the number of research groups focusing on studies with biotrickling filters became internationally significant only in the 1990s [5]. The biotrickling filtration technology was gradually and efficiently implemented at industrial sites, mainly over the past two decades. The first full-scale bioscrubbers were probably installed in the 1970s in German industries (Chapter 6). Activated sludge diffusion is another technology that is suitable for air pollution control and has been used for several decades, mainly at wastewater treatment plants. It has been extensively described elsewhere [1]. That topic is not addressed in this book because little research or new developments have been made over the past 10 years. Membrane bioreactors, which are

**Table 1.5** European emission standards, in  $g\ km^{-1}$ , for gasoline (G) and diesel (D) passenger cars (vehicles of < 2500 kg, laden).

Directive (implementation)	CO		THC		NMHC		NOx		HC + NOx		PM	
	G	D	G	D	G	D	G	D	G	D	G	D
70/220/EEC <sup>a</sup>	<10	–	–	–	–	–	–	–	<2.55	–	–	–
91/441/EEC (1/1/1993) <sup>b</sup>	2.72	2.72	–	–	–	–	–	–	0.97	0.97	–	0.14
94/12/EC (1/1/1996) <sup>c</sup>	2.20	1.00	–	–	–	–	–	–	0.50	0.70	–	0.08
98/69/EC (1/1/2000) <sup>d</sup>	2.30	0.64	0.20	–	–	–	0.15	0.50	–	0.56	–	0.05
98/69/EC (1/1/2005) <sup>d</sup>	1.00	0.50	0.10	–	–	–	0.08	0.25	–	0.30	–	0.025
715/2007/EC (1/9/2009) <sup>e</sup>	1.000	0.500	0.100	–	0.068	–	0.060	0.180	–	0.230	0.005	0.005
715/2007/EC (1/1/2014) <sup>e</sup>	1.000	0.500	0.100	–	0.068	–	0.060	0.080	–	0.170	0.005	0.005

Note: THC = total hydrocarbons; NMHC = nonmethane hydrocarbons; HC = hydrocarbons; PM = particulate matter.

<sup>a</sup>Directive of 20 March 1970 (OJ L76, 6.4.1970, pp. 1–22).

<sup>b</sup>Directive of 26 June 1991 (OJ L242, 30.8.1991, p. 0001–0106).

<sup>c</sup>Directive of 23 March 1994 (OJ L 100, 19.4.1994, pp. 42–52).

<sup>d</sup>Directive of 13 October 1998 (OJ L 350, 28.12.1998, pp. 1–65).

<sup>e</sup>Directive of 20 June 2007 (OJ L 171, 29.6.2007, pp. 1–16).

already used in other areas such as wastewater treatment, are described in Chapter 7. They have, however, not yet been implemented at full scale for waste-gas treatment. Other innovative approaches have been suggested recently such as the two-liquid-phase bioreactors, rotating biological contactors or multistage processes, among others (Chapter 8, Chapter 9 and Chapter 10). Interestingly, for some very important pollutants such as CO or NO<sub>x</sub>, research with bioreactors has been done for several years already at the lab scale, but the technology has hardly been scaled up so far [6–8]. There is certainly room for further studies in that direction.

### 1.3.3 Environmentally friendly bioenergy

Fossil fuels used in combustion processes in either stationary or mobile sources of pollution are known to emit high amounts of particulate matter and volatile organic and inorganic pollutants to the atmosphere (Figure 1.1). This has led to the search for alternative, more environmentally friendly fuels and sources of energy to drive vehicles. The European Emission standards for new gasoline and diesel passenger cars are summarized in Table 1.5, for different directives approved since 1970, showing that overall the emissions have significantly decreased over the past four decades. All these exhaust gases are released through the tailpipes and significantly affect our environment. One alternative to running fossil fuel-powered cars is electric vehicles. The latter do not have any tailpipe. This does, however, not mean that they are not polluting at all, since the production of electric power required to charge the cars' batteries depends on air-polluting processes. Some other drawbacks of electric vehicles should be considered as well, such as their limited driving range, as batteries need to be recharged about every 300–400 km in the best case, based on the presently available technologies.

Other options include using more environmentally friendly (bio)fuels, such as ethanol, methanol, biodiesel, hydrogen and biogas (methane), among others. Several chapters in this book focus on such fuels (Chapter 13, Chapter 14, Chapter 15, Chapter 16, Chapter 17 and Chapter 18). They will thus not be described in detail here. As a general rule, emissions from such fuels are often lower than in the case of fossil fuels, although this is not always the case. One major advantage is that they can often be produced from renewable resources or from waste, wastewater or waste gases.

## 1.4 Conclusions

The most common air pollutants are particulate matter, carbon monoxide, ammonia, nitrogen oxides, sulphur oxides, and volatile organic compounds. They are emitted from either stationary sources or mobile sources. Carbon monoxide is, by far, the most abundant air pollutant, and it is mainly released during combustion processes. Bioprocesses are not suitable for dealing with particulate matter pollution, although several other efficient, nonbiological alternatives are available. All other pollutants can be eliminated biologically or through other physical and chemical techniques. Some of those techniques simply transfer the pollutant from one phase (air or gas) to another (absorption and adsorption, mainly), while others destroy the pollutants (biological and nonbiological degradation or oxidation processes). Actually, bioprocesses can be used both for destroying the pollutant and for their bioconversion into other useful products, which is a quite more recently developed option.

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