Chapter 1
Gaseous Species

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Abstract Gaseous pollutants in East Asia are explained in this chapter. Sulfur dioxide (SO_2) emissions in this region of the world are now decreasing, although these emissions in China are still the highest in the world. SO_2 emission in South Korea decreased very quickly; in Japan, it took about 20 years to reduce the atmospheric SO_2 concentration from 50 ppb to less than 5 ppb, whereas it took only 10 years in Korea to reduce the SO_2 concentration by the same amount, owing to a switch in fuel sources from coal to natural gas.

The emission of nitrogen oxides (NOx = NO + NO_2) is still increasing in China, and this emission causes an increase in tropospheric ozone. The transboundary transport of ozone and its precursors is affecting not only the countries surrounding China, but also North American countries.

Trends in ozone concentrations over the East China Sea were analyzed, based on aerial observations for up to 20 years. A clear increase in ozone was found, particularly in the boundary layer, lower than 1,500 m above sea level.

Keywords SO_2 • NO_2 • Ozone • Air quality standards • Yearly trends • Long-range transport

1.1 Introduction

The economy in Asia is among the most rapidly developing in the world, and economic growth in East Asia is particularly rapid. For example, China's gross domestic product (GDP) was the second highest in the world in 2010. Such economic growth has brought about an increase in fossil fuel consumption and inevitably caused increasing emission of air pollutants. Thus, at the end of the twentieth century, East Asia was responsible for the largest emissions of sulfur dioxide (SO_2) and nitrogen oxides (NOx = NO + NO_2) in the world, exceeding those of the United States and also those of Europe Akimoto 2003; Ohara et al. 2007).

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During the twentieth century, acid rain was often implicated as a cause of forest decline and was considered a global environmental problem. However, the true problem associated with acid rain is not the acidification of rainwater, but rather, the anthropogenic emission of acid raw materials such as SO_2 and NOx as exhaust gases from factories and automobiles. The dissolution of these acidic substances in rainwater forms acid rain, and thus acid rain is a result of air pollution. From this viewpoint, acid rain can be considered a form of long-range, transboundary air pollution. Acid rain problems in East Asia must also be dealt with as phenomena of transboundary air pollution. In North American and European countries, serious acid rain problems were overcome by switching to cleaner fuels, as well as by desulfurization and denitrification technologies, but intercontinental air pollution remains a major environmental issue (UNECE 2011).

The gaseous pollutants often believed to be the sources of acidic substances in the air are SO_2, NOx, and surface ozone. Photochemical oxidation of SO_2 yields sulfuric acid in the air, and this sulfuric acid forms fine particles in its native form and also upon neutralization with ammonia gas (NH_3). Photochemical reactions involving NOx bring about the formation of ozone in the troposphere, and this is the main component of photochemical smog. Photochemical oxidation of NOx also yields nitric acid in the air. The nitric acid forms fine particles upon neutralization with ammonia gas. Damage to plants occurs mostly by acids and gases producing acidic substances. Acids are usually formed as particulate matter, and they will be discussed in further detail in Chap. 2. Typical acid-producing substances are: (1) gaseous precursors of acids, such as SO_2 and NOx, and (2) oxidizing gases and radicals, such as ozone, H_2O_2, and OH radicals. The three gaseous species; namely, SO_2, NOx, and ozone, are strongly related to acid rain problems and also to damage to plants. In this chapter, we discuss these three gases and their prevalence in Asia, particularly in Japan, China, and Korea.

1.2 SO_2

In addition to being emitted by natural processes such as volcanic activity, SO_2 is emitted from anthropogenic sources such as fossil fuel combustion and the smelting of pyrites. A total of 86,273 kt of SO_2 was emitted worldwide from anthropogenic sources in 2010 (Cofala et al. 2012). Emissions from China, Japan, and Korea account for 34 %, 1 %, and 1 %, respectively, of worldwide emissions (Fig. 1.1).

SO_2 causes human health problems, such as asthma; these effects are observed in areas near large-scale SO_2 emission sources. In addition, SO_2 that is oxidized to sulfuric acid (H_2SO_4) in the air can be transported long distances on a regional or continental scale.

Oxidation of SO_2 in the atmosphere takes place in two ways. One is by means of a homogeneous gas-phase process. The main oxidizing agent in the homogeneous gas-phase is OH radicals. OH radicals react with SO_2 as follows:
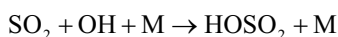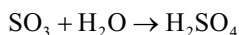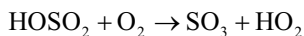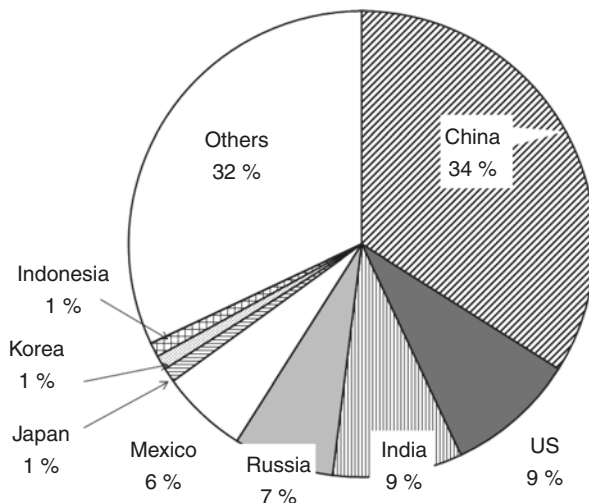
$$SO_2 + OH + M \rightarrow HOSO_2 + M$$

$$HOSO_2 + O_2 \rightarrow SO_3 + HO_2$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

where M is a third body whose purpose is to remove excess energy by means of adduct formation.

The other means by which SO$_2$ is oxidized in the atmosphere is by a heterogeneous reaction on the surfaces of cloud droplets or a homogeneous aqueous-phase process within cloud droplets. Many oxidizing agents have been suggested to promote these types of SO$_2$ oxidation, with the dominant oxidizing agent being H$_2$O$_2$ (Schwartz 1984). H$_2$O$_2$ reacts with HSO$_3^-$ (the dominant chemical form of SO$_2$ dissolved in water at pH less than 5) as follows:

$$HSO_3^- + H_2O_2 \rightarrow A^- + H_2O$$

$$A^- + H^+ \rightarrow 2H^+ + SO_4^{2-}$$
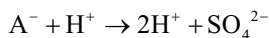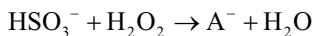
Here A$^-$ is speculated to be O$^-$—S (O)——OOH (Hoffmann and Jacob, 1984).

SO$_2$ and its oxidation product SO$_4^{2-}$ can cause serious environmental problems by forming acid rain in areas far away from SO$_2$ emission sources. Acid rain was thought to be a major cause of forest decline in Europe and North America for a long time.

1.2.1 Japan

In Japan, air pollution by SO$_2$ was most serious in the 1960s and early 1970s. Particularly, around Yokkaichi City many people suffered from a serious respiratory disease that is referred to as Yokkaichi-Zensoku (Yokkaichi asthma); high

concentrations of SO_2 (i.e., annual average concentrations higher than 0.05 ppm) and of its oxidation product H_2SO_4 are considered to be the causes of this disease. In 1973 the Japanese air quality standard for SO_2 was established to lower the SO_2 level. The air quality standard for SO_2 is 0.1 ppm hourly and 0.04 ppm daily, calculated as the average of all hourly averages in one day. Once these standards were established, the ambient SO_2 level in Japan decreased to 0.005 ppm; it has remained at or below this level for 20 years (Fig. 1.2; Ministry of the Environment, Japan 2012, 2015). Both air quality standards for SO_2 were achieved in nearly 100 % of residential areas in 2013.

1.2.2   China

In China, national air quality standards are classified into three grades. Grade I applies to special protected areas, such as natural conservation areas, scenic areas, and historical sites; Grade II applies to residential areas, mixed commercial/residential areas, and cultural, industrial, and rural areas; and Grade III applies to special industrial areas. Chinese standards for the three grades are listed in Table 1.1. In China, 88.2 % of cities achieved the national air quality standards in 2014 (Ministry of Environmental Protection, China 2014).

Lu et al. (2010) estimated that SO_2 emission in China increased from 21.7 Tg in 2000 to 33.2 Tg in 2006, a 53 % increase. They also suggested that emissions began to decrease after 2006 mainly due to the widespread application of flue-gas

Fig. 1.2 Ambient SO_2 levels in Japan (Adapted from Ministry of the Environment, Japan 2012, 2015)
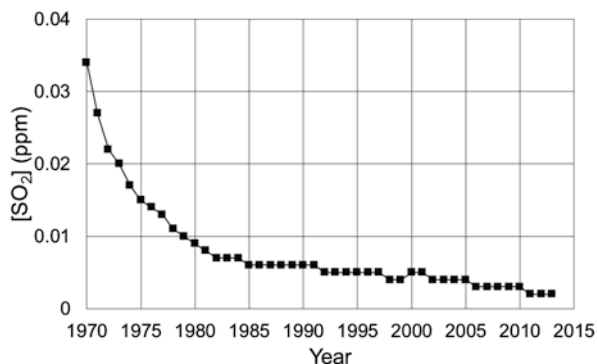
Table 1.1 National air quality standards in China for SO_2 (mg m^{-3})

	Grade I	Grade II	Grade III
Annual average	0.02	0.06	0.1
Daily average	0.05	0.15	0.25
Hourly average	0.15	0.5	0.7

0.1 mg m^{-3} of SO_2 is approximately 38.2 ppb (25 °C)

desulfurization devices in power plants in response to a new policy implemented by China's government. The emission of SO_2 in China has decreased since 2006, as can be seen in Fig. 1.3, in which the graph displays the official SO_2 emission data reported by the Ministry of Environmental Protection of China in their State of Environment report.

One major source of SO_2 emission is power plants. As shown in Fig. 1.4, ~80 % of the electric power generated in China in 2012 came from thermal power plants, and 95 % of that thermal power came from coal combustion (China Electricity Council 2012). Power generation by oil combustion accounted for only 0.14 % of the power generation of thermal power plants with capacity of 6,000 kW and higher in China during that same year. This distribution of power sources can be expected to persist for many years, because oil production in China is limited, whereas coal deposits in China are large. For this reason, the reduction of SO_2 emission remains a major challenge for China.

1.2.3 Korea

In contrast to China, Korea reduced SO_2 emissions very quickly. As shown in Fig. 1.5 (Choi 2014), annual average concentrations of SO_2 in Seoul decreased from ~50 ppb in 1990 to ~5 ppb in 2000. Such a rapid improvement in air quality was attained by the transition to cleaner fuel (Choi 2014). During the 1970s and
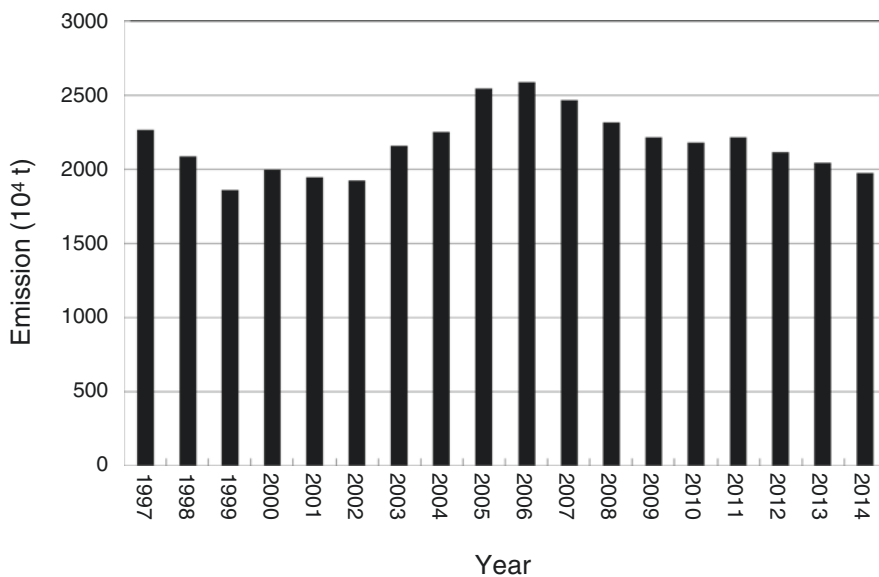

Fig. 1.3 Emissions of SO_2 in China (From the Report on the State of the Environment in China, Ministry of Environmental Protection of China)

1980s, the major SO_2 emission sources in Seoul were fossil fuels, such as coal and oils with high sulfur content. However, the use of solid fuels such as coal and wood for business facilities in the Seoul metropolitan area was prohibited beginning in 1985, and the use of liquefied natural gas (LNG), a cleaner fuel, was mandated. This switch in fuel sources proceeded very smoothly, and both businesses and households in Korea had moved from using wood and coal in the 1960s to using LNG by the 1990s.
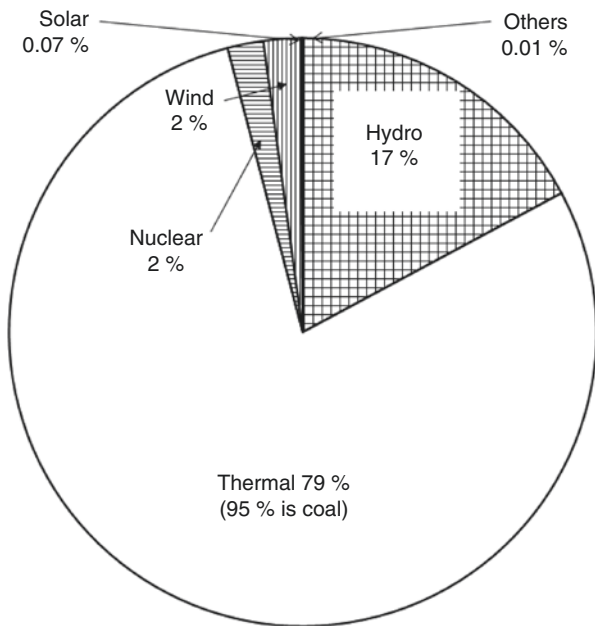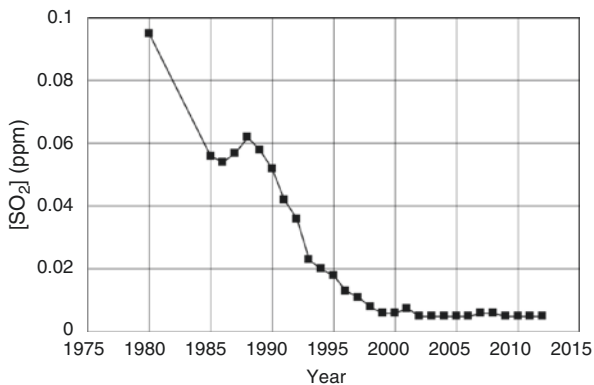

Fig. 1.4 Power generation in China in 2012 (Adapted from China Electricity Council 2012)

Fig. 1.5 Ambient annual SO_2 levels in Seoul, South Korea (Adapted from Choi 2014)

1.3 NOx

The worldwide emission of NOx was determined to be 84,696 Gg in 2010 (Cofala et al. 2012). Countries with particularly high emissions are China, the United States, and India (Figs. 1.6 and 1.7). East Asian countries such as China, Japan, and Korea emitted only 25 %, 2 %, and 1 % of worldwide NOx, respectively.

Although SO_2 is emitted from the combustion of sulfur-containing fuels, particularly coal, NOx is emitted from all types of combustion processes, because NOx is formed mainly by the reaction $N_2 + O_2 \rightarrow 2NO$ at high temperature. This reaction is endothermic, so it generally does not occur at room temperature and regular atmospheric pressure. However, this reaction is accelerated at higher temperatures,

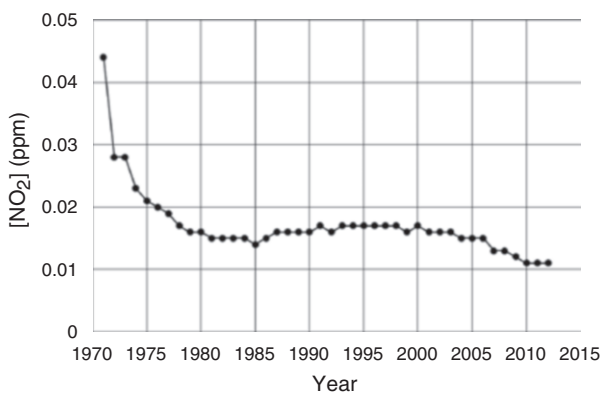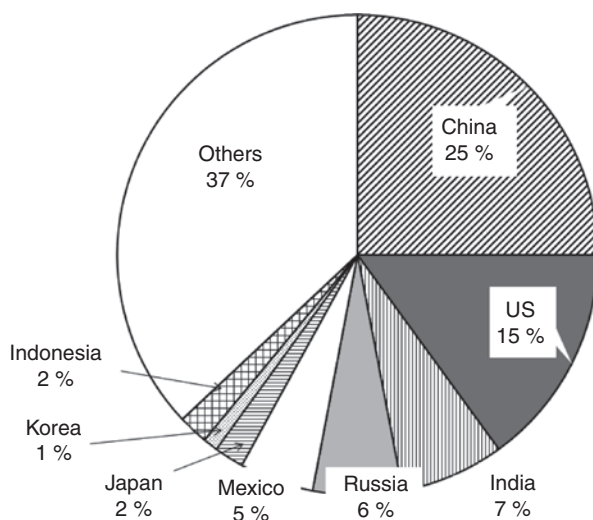**Fig. 1.6** Emissions of NOx by country in 2010 (Adapted from Cofala et al. 2012)

Fig. 1.7 Ambient NO_2 levels in Japan (Adapted from Ministry of the Environment, Japan 2012, 2015b)

particularly those above 1,900 °C. Such high temperatures are found inside internal combustion engines and power station boilers during the combustion of fuels in the presence of air. The emitted NO is then easily converted to NO_2 in air by oxygen molecules, ozone, and peroxy radicals such as HO_2 and RO_2 (where R is an alkyl group). The sum of NO and NO_2 is referred to collectively as NOx. Although NOx is an important atmospheric species that affects atmospheric chemistry, air quality, and climate (IPCC 2013), the most important role of NOx is to control the tropospheric ozone (O_3) budget and the formation of nitrate aerosol. Tropospheric ozone will be discussed in the next section of this chapter, and nitrate aerosol will be discussed in the next chapter. NOx is an important target of air pollution control measures worldwide.

The transport of NOx within East Asia is a substantial problem. Satellite measurements over East Asia (Lee et al. 2014) have clearly shown the high column concentration of NOx over China and the Yellow Sea, suggesting the contribution of NOx transport to downwind regions, in addition to local emissions.

A distinct seasonal cycle of NOx exists in most regions of East Asia (Mijling et al. 2013), as shown by satellite measurements acquired from 2007 to 2011. Van der A et al. (2006) showed that anthropogenic sources caused NO_2 concentrations to peak in winter, whereas soil emissions peaked in summer.

1.3.1 Japan

Air pollution by NOx in Japan was at its most serious in the 1960s and early 1970s. After 1973, when strict regulations for automobile exhausts were enacted, the emission of NOx decreased, and ambient concentrations subsequently decreased, as shown in Fig. 1.6 (Ministry of the Environment of Japan 2012, 2015a). However, after 1985, NO_2 did not decrease further, most likely owing to the increase in the number of cars in use in Japan, although the emission from individual cars decreased due to strict emission regulations.

The Japanese air quality standard for NO_2 is <0.04–0.06 ppm per day, calculated as the average of all hourly averages per day. At present, this air quality standard for NO_2 is achieved in nearly 100 % of residential areas.

1.3.2 China

As with SO_2, China maintains three grades of national air quality standards for NOx, as well as for NO_2. Chinese standards for these three grades are listed in Table 1.2. In 2014, 62.7 % of cities in China achieved these national air quality standards (Ministry of Environmental Protection, China 2014).

Kurokawa et al. (2013) reported that the emission of NOx as NO_2 in China in 2008 was 26,969 Gg (89 % growth compared with emission in 2000). Zhao et al.

Table 1.2 National air quality standards in China for NO_2 (mg m^{-3})

	Grade I	Grade II	Grade III
Annual average	0.04	0.04	0.08
Daily average	0.08	0.08	0.12
Hourly average	0.12	0.12	0.24

0.1 mg m^{-3} of NO_2 is approximately 53.1 ppb (25 °C)

(2013) also estimated NOx emission in China, which was 26,100 Gg in 2010, a major increase from the reported 11,000 Gg in 1995. Quite recently, the emission of NOx in China was reported to have decreased, from 24,043 Gg in 2011 to 20,780 Gg in 2014 (Ministry of Environmental Protection, China 2014). As suggested by Zhang et al. (2007), the reason for this observed decrease could be the installation of low-NOx boilers, especially in new large power plants. Nevertheless, because it has also been reported that the number of privately owned automobiles in China has increased to 100 million (China Daily 2011-09-17), and that this number continues to increase (Statista 2015), trends in NOx emission should be monitored more carefully.

The increase in NOx column abundance from 1996 to 2004 was observed clearly through satellite observations. In particular, the increment of NOx column abundance over the Beijing, Jinan, and Shanghai areas is as high as 8×10^{14} molecules cm^{-2} year^{-1} (van der A 2006).

Wang et al. (2012) estimated the contributions of six major sources (power plants; biomass burning; soils and fertilizers; lightning; aircraft; and other anthropogenic sources, including industry, transportation, and biofuels) of NOx emission in 2007 to be 9.58, 0.23, 1.77, 0.59, 0.05, and 13.77 Tg NO_2, respectively, based on the Goddard Earth Observing System (GEOS)-Chemistry model. Biomass burning is an unimportant source of NOx in East China, contributing less than 1 % to total NOx emissions.

1.3.3   Korea

Korean air quality standards for NO_2 are 0.03, 0.06, and 0.10 ppm for annual, daily, and hourly average emissions, respectively. The national annual average air pollution level of NO_2 has been maintained below the air quality standard of 0.03 ppm (which was enacted in 2007). However, NO_2 emissions have improved only slowly in Seoul, where the annual average exceeded 0.03 ppm between 1999 and 2011 before the air quality standard was achieved in 2012 (Choi 2014). Key measures responsible for this improvement included switching to clean heating fuel (coal → oil → natural gas), introducing and strengthening emission standards for motor vehicles since 1991, and promoting the use of low-emission vehicles.

Nguyen et al. (2015) analyzed the long-term trends of NO_2 emission in seven major Korean cities over two decades (1989–2010). Because notable environmental policies were initiated in June 2000, these investigators divided the observation

period into period I (1989–1999) and period II (2000–2010). They found that the mean concentrations of NO_2 in five cities were 1–26 % higher in period II than in period I. For example, the annual average concentrations of NO_2 in period I and period II were 31.2 and 36.1 ppb, respectively, in Seoul; 24.2 and 25.3 ppb, respectively, in Daegu; and 17.0 and 21.5 ppb, respectively, in Gwangju. This increase is thought to be due to the increasing consumption of petroleum and LNG. In Busan and Ulsan, lower concentrations of NO_2 were observed in period II than in period I.

As briefly mentioned under the heading 'NOx' above, the transport of NO_2 in East Asia is a very important phenomenon for Korea and Japan. Monthly variations in NO_2 columns, as measured by the Ozone Monitoring Instrument (OMI) satellite instrument over China and Eastern China clearly show a strong winter maximum, whereas over the Yellow Sea, Korea, the Sea of Japan, and Japan, an NO_2 peak is observed in spring and early summer (March–June; Lee et al. 2014). Surface observations of NO_2 in Korea show a similar spring peak. Because the springtime NO_2 enhancement agrees with the maximum CO observed at remote sites, despite the lifetime of CO being much longer than that of NO_2, Lee et al. (2014) suggested that NOx could be transported by a means similar to that of CO.

1.4 Tropospheric Ozone

Ozone (O_3) is a major air pollutant that is known to exist both in the stratosphere and in the troposphere. In the stratosphere, ozone is formed mainly by the Chapman mechanism, as follows:

$$O_2 + h\nu \rightarrow 2O \tag{1.1}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{1.2}$$

$$O_3 + O \rightarrow 2O_2 \tag{1.3}$$

$$O_3 + h\nu \rightarrow O + O_3 \tag{1.4}$$

where h is Plank's constant, ν is the frequency of light, and M is a third body that removes excess energy from O_3.

As long as ozone is present only in the stratosphere, it is valuable not only for human beings but also for all the living things on the surface of the earth, because it blocks high-energy ultraviolet (UV) light, i.e., that with wavelengths shorter than 300 nm. However, ozone is a toxic gas, and so it is not desirable for ozone to exist at high concentrations in the lower troposphere. High ozone concentrations are harmful to respiration and lung function in humans (Bernard et al. 2001; Bell et al. 2007; Amman et al. 2008). Ozone also has detrimental effects on plants, the details of which will be discussed in later chapters.

High concentrations of ozone are often produced as the result of photochemical smog formation processes. Therefore, ozone is considered to be a major air pollutant.

Moreover, ozone is now recognized as a strong greenhouse gas. The atmospheric lifetime of ozone is much shorter than that of CO_2, but ozone can still induce regional warming and climate change (IPCC 2013).

In the lower troposphere, which is not penetrated by high-energy UV light, the only source of O_3 is the photolysis of NO_2 and subsequent reactions, as follows:

$$NO_2 + h\nu \rightarrow NO + O \tag{1.5}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{1.2}$$

$$O_3 + NO \rightarrow NO_2 + O_2 \tag{1.6}$$

Since NO_2 is brown, it can absorb visible light within the wavelength region of 450–700 nm and subsequently decompose to form NO and an oxygen atom, as shown in Reaction 1.5 above. An oxygen atom then reacts with an oxygen molecule to form O_3 in the same manner as in the stratosphere. Thus, NO_2 alone can form ozone in the troposphere. However, NO_2 alone cannot produce high concentrations of O_3, such as those seen in photochemical smog, because NO can destroy O_3 by means of Reaction 1.6. This reaction is referred to as a titration reaction of NO for ozone.

In the atmosphere, there are many kinds of volatile organic compounds (VOCs), most of which are hydrocarbons. Under photochemical smog conditions, gas-phase chemical reactions take place mainly as OH-radical-initiated reactions, and these reactions produce the peroxy radicals HO_2 and RO_2 (where R is usually an alkyl group). HO_2 or RO_2 can readily react with NO to form NO_2 without destroying O_3. A schematic diagram of the formation of ozone in the absence and in the presence of VOCs is shown in Fig. 1.8.

Mechanisms of reactions influencing atmospheric ozone are described in detail in a recent publication by Calvert et al. (2015).

1.4.1 Japan

In Japan, the air quality standard for ozone is included in that for general photochemical oxidants, since the initial official measurement method was based on a wet chemical method utilizing iodometric analyses, which can be used to detect both
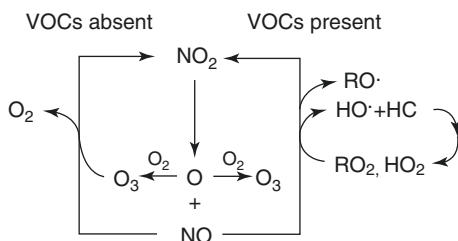

Fig. 1.8 Formation of ozone in the absence and the presence of volatile organic compounds (VOCs)

ozone and other gaseous oxidative compounds. However, UV absorption and chemiluminescence methods are now the official means for monitoring photochemical oxidants in Japan, and most monitoring is now achieved by these dry methods. Therefore, we may consider the officially reported concentrations of photochemical oxidants in Japan to be equivalent to the concentrations of ambient ozone. The air quality standard for photochemical oxidants (ozone) is 0.06 ppm (hourly average).

Photochemical smog in Japan was a very serious problem in the late 1960s and early 1970s. After the strict regulation of NOx emission from automobiles started in 1973, as described above Sect. 1.3.1, the concentration of photochemical oxidants decreased remarkably by 1980 (Fig. 1.9; Ministry of the Environment, Japan 2015a). However, the photochemical oxidant concentration gradually increased after 1980, although the concentration of an important ozone precursor, NO_2, decreased over the same time period. In addition, the concentration of VOCs has also been decreasing. Therefore, the increase in the photochemical oxidant concentration is mysterious. The reduction of NOx from automobile exhausts is assumed to be one cause of this increase: such reduction is believed to decrease the efficiency of the titration reaction by NO. Another important cause of the gradual increase of photochemical oxidants is the transport of ozone or its precursors from China (e.g., Yoshitomi et al. 2011).

The low rate of achievement of the air quality standard for photochemical oxidants is another big problem in Japan. The percentages of monitoring stations in Japan that showed concentrations lower than the air quality standard in 2012, 2013, and 2014 were 0.5 %, 0.3 %, and 0.3 %, respectively (Ministry of the Environment, Japan 2015b). One important factor is that the Japanese air quality standard for photochemical oxidants is very strict: Japan's hourly average standard is only 0.06 ppm, whereas those for the United States and Korea are 0.1 and 0.12 ppm,
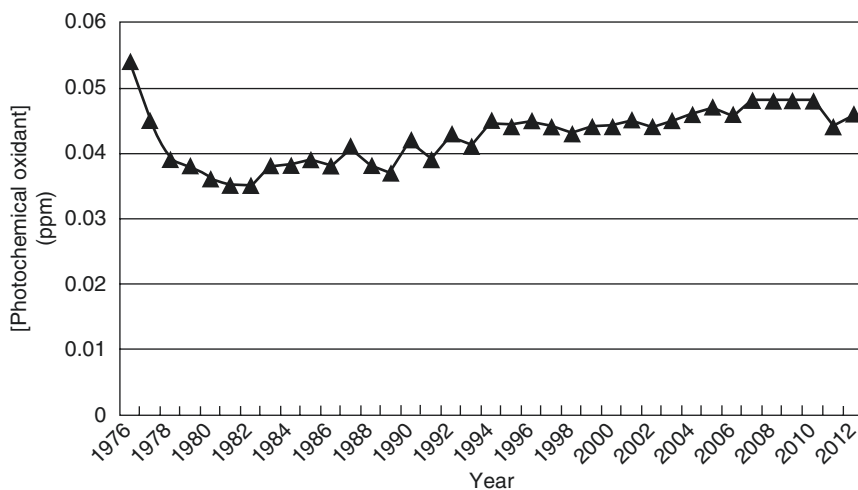

Fig. 1.9 Ambient photochemical oxidant levels in Japan (adapted from Ministry of the Environment, Japan 2015b)

respectively. China has three grades of standards, as described in the next section. Moreover, if the hourly average concentration of photochemical oxidants at a given monitoring site in Japan exceeded 0.06 ppm even once over the course of a year, that monitoring site was reported as not having achieved the standard. In contrast, among the 1,152 monitoring stations in residential areas in Japan, a total of 93.2 % reported daytime photochemical oxidant levels lower than 0.06 ppm in 2013.

1.4.2   China

As with SO_2 and NO_2, national air quality standards for ozone are classified into three grades in China. The Chinese standards for these three grades are listed in Table 1.3. In 2014, 78.2 % of cities in China achieved these national air quality standards (Ministry of Environmental Protection, China 2015).

Recently, Verstraeten et al. (2015) showed that tropospheric ozone concentrations over China had increased by about 7 % between 2005 and 2010 in response to two factors: an approximately 21 % increase in Chinese emissions and the increased downward transport of stratospheric ozone. The same report also stated that ozone from China affects air quality in the United States.

Annual average concentrations of ozone in China in 2013 and 2014 were 139 and 140 µg m^{-3}, or ~70.8 and ~71.3 ppb, respectively, at 25 °C (Ministry of Environmental Protection, China 2014, 2015).

Yoshitomi et al. (2011) estimated that the Chinese contribution to surface ozone over Japan in the spring season was 4.0 ± 2.8 ppb, which was larger than the European and North American contributions (3.5 ± 1.1 and 2.8 ± 0.5 ppb, respectively). This Chinese contribution could be expected for a closer source region, and levels are generally highest near cold fronts preceding the influence of more distant sources. Local sources over Japan and Korea have been reported to have a relatively small impact on the mean ozone level over Japan, at 2.4 ± 7.6 ppb, respectively.

1.4.3   Korea

Korean air quality standards for ozone are 0.06 and 0.1 ppm for daily and hourly averages, respectively. Annual averages of ozone for Korea were 0.020, 0.020, 0.022, 0.023, and 0.026 ppm in 1998, 2000, 2005, 2010, and 2013, respectively (Ministry of Environment of Korea 2015). Ozone is said to have been maintained

Table 1.3 National air quality standards in China for O_3 (mg m^{-3})

	Grade I	Grade II	Grade III
Hourly average	0.12	0.16	0.20

0.1 mg m^{-3} of O_3 is approximately 50.9 ppb (25 °C)

below the air quality standards for the past two decades. In the Seoul metropolitan area, the average concentration of ozone is also low (Choi et al. 2014). Seo et al. (2014) pointed out that O_3 levels for coastal cities are high due to the dynamic effects of the sea breezes, while the levels for inland cities and the Seoul metropolitan area are low due to NOx titration by local precursor emissions. However, the annual average concentration of O_3 in Seoul is on the rise (Choi et al. 2014).

1.4.4 *Trends in Ozone Concentrations Above the East China Sea Based on Aerial Observations*

In this section, trends in ozone concentrations over the East China Sea are discussed based on 20 years of aerial observations carried out by the authors. Data used for the analysis are those obtained in the Perturbation of East Asian Continent Air Mass to Pacific Ocean Troposphere (PEACAMPOT) campaign in October 1991, November 1992, March and December 1994, January and December 1997, February 1999, and March 2001; in the Lagrangian Experiment on Long-Range Transported Aerosols (LEXTRA) campaign in March-April 2008; and in the Impact of Aerosols in East Asia on Plants and Human Health (ASEPH) campaign in October 2009 and December 2010, for a total of 11 datasets (Hatakeyama 2000; Hatakeyama et al. 1995a, 1995b, 1997, 2001, 2004, 2011, 2014). Aerial observation is an event-based experiment, and thus the period, season, and area of observation are different every time, which can present challenges in evaluating long-term trends. However, aerial observations are seldom carried out over almost the same area for 20 years, as was done here. Recently, Clarke et al. (2010) reported many aerial observations carried out above oceans all over the world; but those observations were not carried out for the duration of the observations described here. Thus, we can say that our observations provide a unique and valuable dataset. The trends of ionic species observed in these measurements will be discussed in the next chapter; in this section, only the trends in ozone are discussed.

Ozone data were divided into two groups; namely, data from 1991 to 1999 and data obtained after 2000. These two periods, i.e., before and after the year 2000, were analyzed. Before 2000, the concentration of ozone was most frequently in the range of $40 < O_3 < 45$ ppb, whereas after 2000, it was most frequently in the range of $65 < O_3 < 70$ ppb. The results suggest that high concentrations of ozone were present more frequently after 2000, even after accounting for the fact that the number of springtime observations was larger after 2000. The reason for such a shift in the
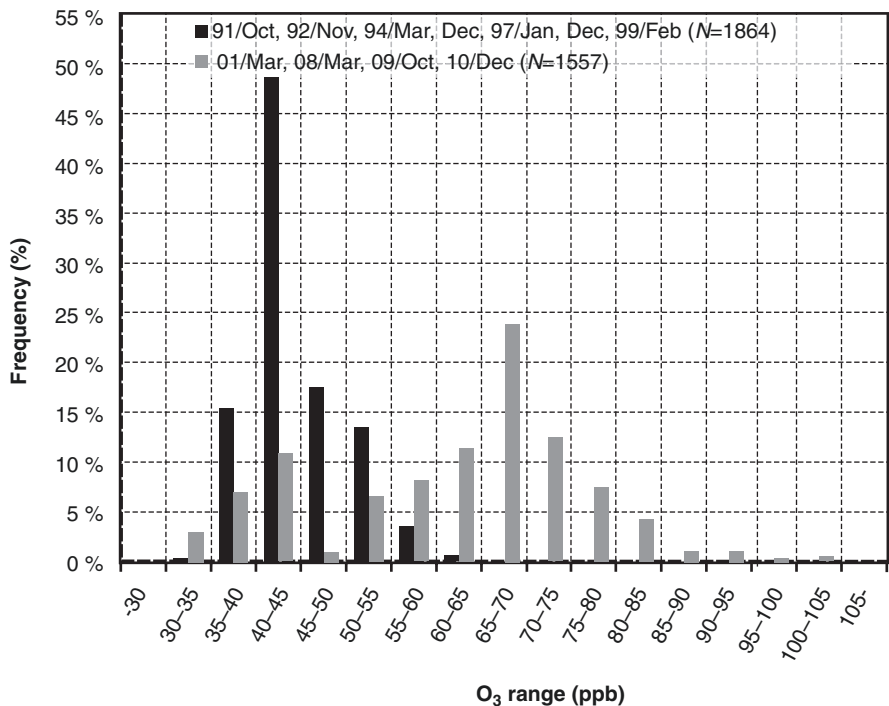
Fig. 1.10 Frequency distribution of ozone concentrations for two time periods (before and after 2000) at altitudes below 1,500 m above sea level

frequency of high-concentration ozone observations is likely an increase in NOx emissions from the Asian continent. In May 2007, high concentrations of ozone, up to 120 ppb in Kyushu and the area facing the Sea of Japan, were observed. Hayasaki et al. (2008) reported that the contribution of transboundary transport to this ozone measurement was large.

Data in the boundary layer below 1,500 m and those in the free troposphere above 1,500 m are shown as histograms in Figs. 1.10 and 1.11, respectively. The above-mentioned trend can also be seen in both atmospheric layers. However, the difference between the two periods is more prominent in the boundary layer. In the free troposphere, the mode appeared at $40 < O_3 < 45$ ppb for both periods, suggesting that the ozone being transported from the upper layer to the boundary layer remains relatively stable, whereas the ozone produced in the boundary layer by human activity is growing.
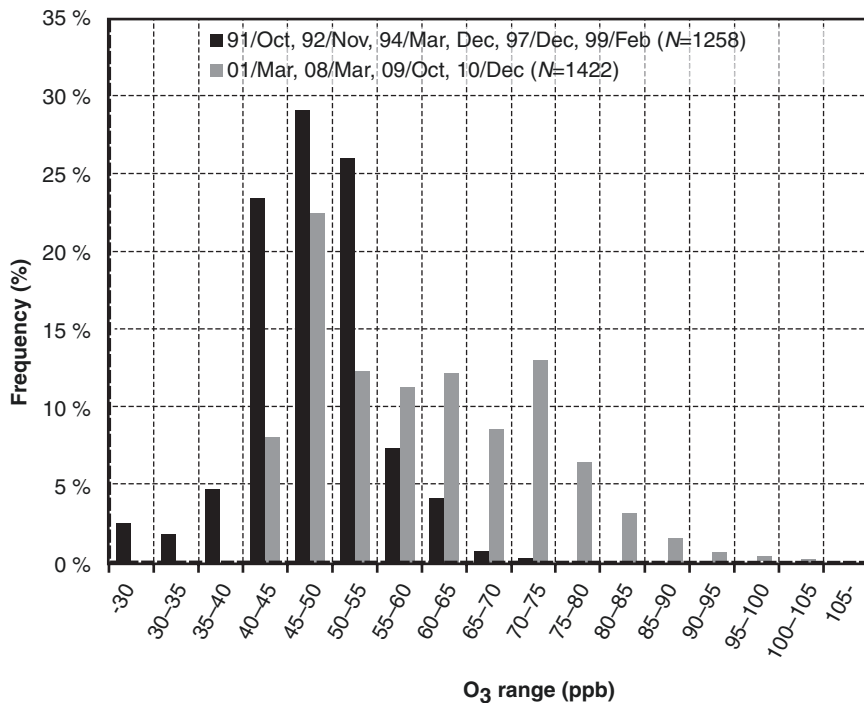
Fig. 1.11 Frequency distribution of ozone concentrations for two time periods (before and after 2000) at altitudes between 1,500 and 3,000 m a.s.l

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