Tropospheric Ozone
A Growing Threat

Acid Deposition and Oxidant Research Center

Foreword

Decreasing concentrations of ozone in the stratosphere are causing a serious problem of depletion of the ozone layer. Meanwhile, ozone concentrations are increasing in the troposphere—the ozone within about ten kilometers from the Earth's surface. A strong oxidant, tropospheric ozone is harmful to humans and ecosystems. It is also a powerful greenhouse gas. Average concentrations of ozone are increasing in Japan and other countries. Even in remote places like the Oki islands in the Sea of Japan, far from any urban center, ozone concentrations in air transported from far away sometimes exceed environmental standards in Japan.

Ozone is produced from the photochemical reaction of nitrogen oxides (NOx) and volatile organic compounds (VOCs) under sunlight. Those pollutants are emitted from automobiles and industries. Since the emission of nitrogen oxides in East Asia is rapidly increasing due to a rapid rise in the use of automobiles, the concentrations of tropospheric ozone are predicted to increase in the future.

Experiments in Europe, the United States and Japan indicate that yield losses of agricultural crops and suppression of tree growth may occur even in under current ozone concentrations. It is projected that if concentrations continue to rise in East Asia, vegetation will be exposed to higher levels of ozone stress, and economic losses will affect not only Japan but also China, the Republic of Korea and other countries in this region.

During the summer seasons in the 1970s, Japan experienced serious problems from pollution by photochemical oxidants, which are composed mainly of ozone. After concentrations gradually decreased, the problems were generally considered to be resolved. However, since around 1980, average ozone concentrations have again been on an increasing trend year-round. This problem is beginning to appear as a global environmental issue, not simply a local one.

Meanwhile, noticing that humans and plants may be affected by long-term exposure to ozone, even in comparatively low concentrations, European and North American countries have developed new environmental standards and indexes. Cooperation among contracting parties in the Convention on Long-Range Transboundary Air Pollution is another example of efforts to reduce precursor pollutants. Some voices are starting to call for efforts to address ozone exposure as a hemispheric issue. Today's issue of tropospheric ozone deserves to be recognized as a transboundary environmental issue. In that context, an appropriate framework is needed so that East Asian countries can also cooperate to tackle this problem.

References

Akimoto, H., Impacts of ozone pollution from East Asia on Japan (in Japanese), Measures of Resources and the Environment, pp. 90-96, Vol.39, No.11, 2003.

Ozone and photochemical oxidants

"Ozone" (O_3, a molecule formed by three atoms of oxygen) is a gas that is harmful to human health. "Oxidant" is a general term for oxidizing substances in the atmosphere. With the exception of nitrogen dioxide, these oxidants are known as "photochemical oxidants." Ozone is the main component of photochemical oxidants, which also contain peroxyacetylnitrate (PAN) and other substances. Damage to plants is expressed differently by ozone and PAN. With lettuce, for example, ozone causes spots to appear on the tips of leaves, while PAN discolors the leaf joints.

Japan has established environmental quality standards for photochemical oxidants, treating it as a major air pollutant. The standards defined photochemical oxidants as "all oxidizing substances that free iodine from neutral potassium iodide solution," and originally required measurement by spectrophotometry and that solution. However, it was later clarified that concentrations of PAN are generally much lower than those of ozone and that PAN is less sensitive to spectrophotometry using neutral potassium iodide than ozone. Meanwhile, it was found that other measurement methods of ozone concentrations, such as by photometric method using ultraviolet, are advantageous in terms of procedures and maintenance. Considering these facts and developments overseas, on 25 October 1996 the then-Environment Agency (later promoted to Ministry of the Environment) notified the governors of Japan's prefectures and mayors of the country's major cities that photometric methods using ultraviolet light can be used to measure photochemical oxidant levels.

"ppm" and "ppb"

Both "ppm" and "ppb" are units used to indicate the presence or concentration of a substance. "ppm" means parts per million and "ppb" parts per billion. Therefore, 1 ppm is equivalent to 1,000 ppb. The relation between "ppm·h" and "ppb·h" ("h" means hour) is similar: 1ppm·h is equivalent to 1,000 ppb·h. This booklet uses whichever unit is appropriate in the discussion, depending on the number of significant figures.

Photochemical oxidant warnings and serious warnings in Japan

"Photochemical Oxidant Warnings" are issued to prevent damage to human health and the environment when hourly concentrations of photochemical oxidants exceed 0.12 ppm and such conditions are expected to continue, based on meteorological conditions. Governors of prefectures inform the general public of the warnings through the media, including television and radio, and seek cooperation to mitigate the problem, for example by asking factories to take measures to reduce the emissions from stationary sources, and drivers to refrain from using automobiles (Paragraph 1, Article 23 in the Air Pollution Control Act).

On the other hand, regulations concerning "Photochemical Oxidant Serious Warnings" are stipulated in guidelines issued by prefectures and other local authorities. These warnings are generally issued when the hourly concentrations of photochemical oxidants exceed 0.24 ppm and such conditions are expected to continue, based on meteorological conditions.

Many municipalities also use the terminology of "Photochemical Smog Warnings" and "Photochemical Smog Serious Warnings."

1. Increasing Tropospheric Ozone

■Stratospheric ozone and tropospheric ozone

Many people know about ozone in the atmosphere, but while they are most likely thinking about "stratospheric" ozone, "tropospheric" ozone is not so well known. However, considering the importance of its direct effects on humans and vegetation, the environmental issue of tropospheric ozone is likely to become a greater concern in the future. About 90 percent of ozone in the atmosphere on the Earth is found in the stratosphere, with approximately the remaining 10 percent in the troposphere. Although both are ozone, its effects on the global environment are quite different depending on where it is found.

With regard to physical properties, ozone has bands of absorption in both the ultraviolet and infrared spectra. Stratospheric ozone absorbs ultraviolet rays in sunlight and prevents them from reaching the surface of the Earth. The ultraviolet light blocked by stratospheric ozone is harmful for living things, and it is commonly known as "good ozone." The loss of this ozone, caused by chlorofluorocarbons (CFCs) and other substances, constitutes a serious problem for the global environment.

In contrast, tropospheric ozone absorbs infrared rays emanating from the Earth and works as a powerful greenhouse gas. The greenhouse effect of this ozone is more significant in the upper troposphere than in other layers. According to the Intergovernmental Panel on Climate Change (IPCC 2001), tropospheric ozone is regarded as the third most powerful greenhouse gas in the atmosphere, after carbon dioxide and methane. Meanwhile, in terms of chemical properties, ozone is a strong oxidant. At the ground level, it is a major air pollutant, and one of the main oxidants. It is also known to cause photochemical smog, which disturbs human respiratory functions and plant photosynthesis. Due to its greenhouse effect and toxicity, tropospheric ozone is known as "bad ozone."

The sources of tropospheric ozone are (1) influx from the stratosphere and (2) generation by photochemical reactions in the troposphere. The influx of ozone from the stratosphere takes place mainly in middle and high latitudes and is most active in early spring. The generation of ozone in the troposphere is most active in summer, since it is caused by photochemical reactions involving nitrogen oxides (NOx), carbon monoxide (CO) and volatile organic compounds (VOCs). Meanwhile, ozone disappears as a result of photochemical reactions with HOx (OH + HO_2) radicals, etc., over the ocean, where NOx concentrations are generally low, and through decomposition by contact with the ground. The amount of ozone generated by photochemical reactions in the troposphere is much greater than the influx from the stratosphere, although the global average net amount of ozone supplied by both sources is about the same, after counting the amount removed by decomposition in the troposphere. Figure 1-1 shows the results of computer modeling of the distribution of ozone concentrations at ground level in a recent year. It reveals that ground-level ozone concentrations are high in middle and high latitudes of the northern hemisphere, especially in regions where air pollutant emissions from human activities are large in volume.

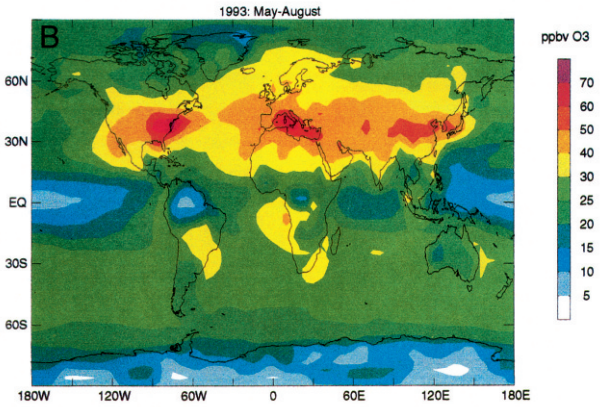

Figure 1-1. Global distribution of ground-level ozone concentrations based on computer model (May-August 1993). (Lelieveld and Dentener 2000)

References

IPCC, "Climate Change 2001," P. 7, 2001.

Lelieveld, J. and F. Dentener, Journal of Geophysical Research, 105, 3531-3551, 2000.

Note: "Radicals"-In atoms and molecules, electrons generally exist in the orbit in pairs. If one of the two is lost, the atom or molecule becomes extremely unstable and chemically active. A radical is an atom or molecule in this condition.

Rising tropospheric ozone concentrations worldwide

As shown on the preceding page, because the amount of ozone generated by photochemical reaction of air pollutants is much larger than the inflow from the stratosphere, the concentrations of ozone are strongly affected by human activities.

How did tropospheric ozone concentrations increase globally as societies became more industrialized? Figure 1-2 plots springtime ozone concentrations at ground level in middle and high latitudes, using data from Europe and Japan from the end of nineteenth century to the present. The figure shows that the concentrations of ground-level ozone were around 10 ppb in Europe at the end of nineteenth century. By contrast, ozone concentrations in rural areas of Europe and Japan in the recent years have reached averages of 40 to 50 ppb from spring to summer. These facts mean that ground-level ozone concentrations have increased to four to five times the levels in the preindustrial era. On the other hand, some argue that data suggesting concentrations of 10 ppb at the end of nineteenth century may have some faults in measurement, because the modeling suggests that ground-level ozone concentrations exceeded 20 ppb even if the anthropogenic emissions of ozone precursors like NOx and VOCs are set at zero, as they would have been in the preindustrial era. Nevertheless, even if ozone concentrations were as high as 20 ppb at the time, recent ozone concentrations at remote and rural sites in the northern hemisphere have at least doubled since the preindustrial era.

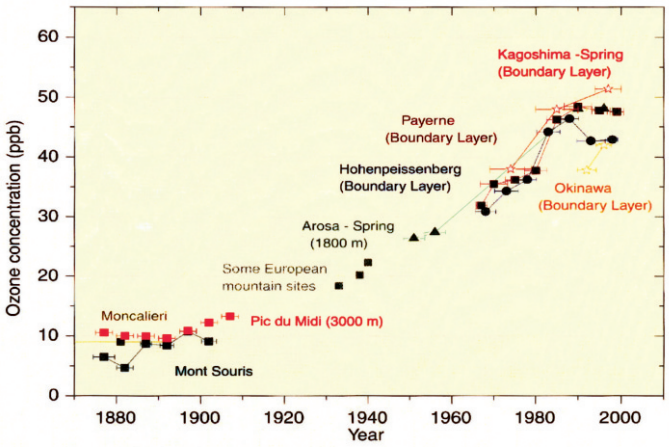

Figure 1-2. Trend of springtime ground-level ozone concentrations in middle and high latitudes of the northern hemisphere from the nineteenth century to the present. (Akimoto 2002)

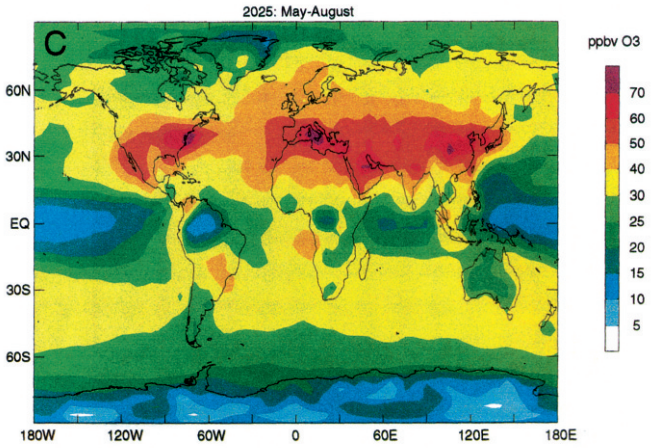

Figure 1-3. Modeling prediction on geographical distribution of ground-level ozone concentrations in 2025 (average from May to August). (Lelieveld and Dentener 2000)

If human activities continue to cause emissions of pollutants that generate ozone, what will happen to ground-level ozone concentrations in the future? Figure 1-3 is one example of modeling predictions for tropospheric ozone. It shows that the average concentration of ozone in North America, Europe and East Asia, including Japan, from May to August will likely exceed 60 ppb, which would exceed accepted levels under Japan's current environmental quality standards. To avoid such a situation, it is urgent to consider countermeasures.

References

Akimoto, H., Chemistry of the troposphere and global environment (in Japanese) (edited by Akimoto H., Kawamura K., Nakazawa T. and N. Washida, p. 97, Gakkai Shuppan Center, 2002.

Lelieveld, J. and F. Dentener, Journal of Geophysical Research, 105, 3531.

Rising concentrations of ground-level ozone in Japan

As mentioned above, tropospheric ozone concentrations have been increasing globally and there are concerns that they may continue to increase in the future. What is the situation in Japan? Figure 1-4 shows the trend of photochemical oxidant concentrations measured at air pollution monitoring stations in Japan, mostly in urban areas. Ozone is considered the primary photochemical oxidant. A comparison of average concentrations between 1985 to 1990 and 1994 to 2002 shows an increase of about 3.5 ppb, which has been observed all over Japan. Ozone concentrations monitored at remote sites in Japan also show an upward trend since 1990. The increases in average ozone concentrations for the ten years from 1992 to 2002 in Happo (a mountainous area) and Ryouri (a coastal area) were 9.0 ppb and 7.3 ppb, representing annual increases of 2.0 and 2.1 percent, respectively.

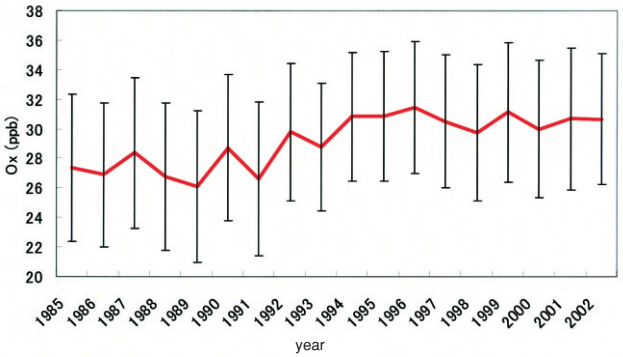

Figure 1-4. Yearly average daytime concentrations of photochemical oxidants in Japan (326 continuous ambient air pollution monitoring stations nationwide). Vertical bars show standard deviation. (Based on Ohara and Sakata 2003)

In the Tokyo metropolitan area as well, concentrations of photochemical oxidants are increasing. According to a survey by the Bureau of Environment of the Tokyo Metropolitan Government (2005), daytime concentrations of photochemical oxidants increased by 5.6 ppb (about a 0.5 ppb increase per year) from 1990 to 2002. Since 2000, the number of days of photochemical smog warnings per year has been increasing, as has the number of days when photochemical oxidant concentrations were 120 ppb or higher. Today, photochemical oxidants reach high levels more often than in the late 1970s (Figure 1-5). In fact, in July 2002, Chiba Prefecture, also located in the Tokyo metropolitan area, issued a photochemical smog serious warning for the first time since 1984. In September 2005, Saitama Prefecture issued a similar serious warning and some damage was reported from the smog conditions. Possible causes of these increases in photochemical oxidant concentrations include (1) meteorological changes, including changes in temperature and solar radiation, (2) an increase in the ratio of VOCs to NOx, and (3) an increase of transboundary air pollution. However, it is not yet clear which factors are actually at work and how they are doing so. Quantitative analysis is therefore urgently needed in order to develop effective countermeasures.

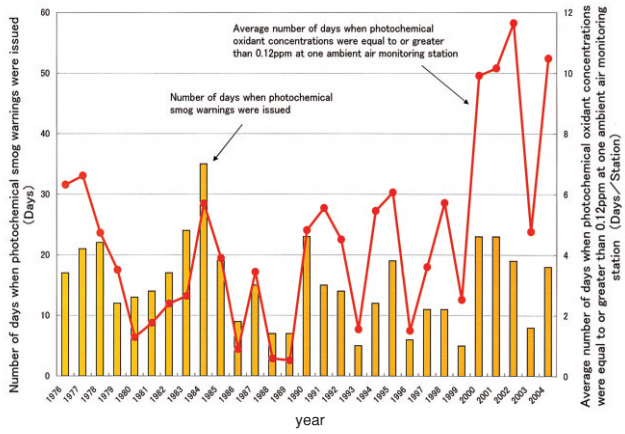

Figure 1-5. Photochemical smog warnings and days with photochemical oxidant concentrations of 0.12 ppm or higher in Tokyo. (Bureau of Environment, Tokyo Metropolitan Government 2005)

References

Bureau of Environment, Tokyo Metropolitan Government, Report of the Committee on Measures about Photochemical Oxidants, 2005.

Ohara , T. and T. Sakata, Journal of Japan Society for Atmospheric Environment (in Japanese), 38, 47-54, 2003.

How is tropospheric ozone formed?

Tropospheric ozone (O_3) is principally generated through photochemical reactions involving nitrogen dioxide (NO_2) (Figure 1-6). It is formed by a reaction between oxygen molecules (O_2) and oxygen atoms (O) released when NO_2 reverts to nitrogen monoxide (NO) through photolysis under the influence of ultraviolet light from the sun.

In a chamber containing clean air and nitrogen oxides (NOx), after O_3 decomposition ($O_3 + NO \rightarrow O_2 + NO_2$), an equilibrium of generation and decomposition reactions will be reached when the ozone concentration reaches 10 to 20 ppb at most. However, if volatile organic compounds (VOCs) are added to that chamber, VOCs react with atoms of oxygen (O), O_3 and OH radicals in the oxidation process under sunlight, to generate oxide radicals (RO) and peroxide radicals (HO_2, RO_2, RCO_3), which play a role in re-producing NO_2 from NO. Among various types of VOCs, olefins (one group of hydrocarbons) generally have strong photochemical activity, followed by alkyl benzene and paraffin (another group of hydrocarbons). The two latter substances contribute significantly to the regeneration of NO_2, since they exist in high concentrations in the atmosphere.

The formation of NO through photolysis and the regeneration of NO_2 from the newly produced NO by peroxide radicals constitute one cycle, in which one molecule of ozone is produced. The peroxide radical functions as a kind of catalyst, since it reverts to its original form quickly after reduction.

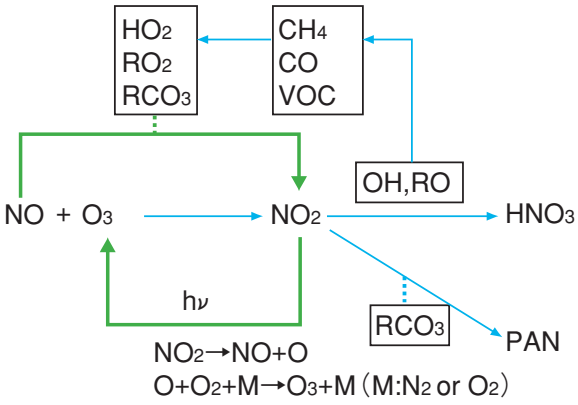

Figure 1-6. Generation and transformation process of ozone and nitrogen compounds.
O_3 is formed through the photolysis of NO_2. The production of NO_2 is caused by O_3 and peroxide radicals. NO_2, reacts again to become HNO_3 and PAN.
Note: R indicates alkyl group, aryl group, etc. PAN indicates peroxyacetylnitrate.

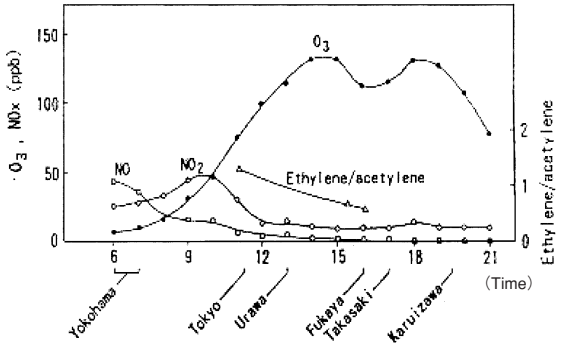

Figure 1-7. Behavior of ozone and its precursors in a polluted air mass over a long distance. (Carmichael et al. 1994).

Ozone concentrations increase in proportion to differences in the rates of formation and decomposition (i.e., the net rate of formation). One study monitored polluted air masses moving from the Tokyo metropolitan area to the Chubu mountain area in Japan on a sunny day in summer (Figure 1-7). In the early morning, NO was in high concentrations in a polluted air mass above Tokyo Bay and the coastal area. It began to be transformed to NO_2 at sunrise. After further photochemical reactions, the NOx concentrations (the total of both substances) declined rapidly after about nine o'clock in the morning, and they were transformed into HNOx, nitrate aerosols and PAN. At that time, the ratio of ethylene/acethylene concentrations (an indicator of photochemical activity) also declined rapidly while ozone concentrations increased sharply. At around 2 o'clock in the afternoon, when the air mass reached Urawa and Fukaya, dozens of kilometers downwind from the emission sources, ozone concentrations peaked and the air mass continued traveling to the Chubu mountain area with those high ozone concentrations.

Initial concentrations and the ratio of NOx and VOCs near the emission sources have a great influence on the amount of photochemical ozone production as well as its geographical distribution. When the NOx/VOC ratio is higher than around 0.1 ppb/ppbC, the amount of ozone produced depends largely on VOC concentrations, and not so much on NOx concentrations (and vice versa). This means that measures to reduce NOx and VOC emissions will have different results, depending on the NOx/VOC ratio in the vicinity of emissions sources. In addition, when the proportion of VOCs is large, ozone concentrations will increase in early hours of the day, with the result that high ozone concentrations will be observed near the emission sources.

2. NOx and VOCs Increasing in Asia

Rising NO_2 concentrations (evidence by satellite data)

It is thought that emissions of NOx, which lead to the formation of ozone, are increasing dramatically in Asia as the region experiences rapid industrialization. The Global Ozone Monitoring Experiment (GOME), which observed the distribution of NO_2 column concentrations in the troposphere, provided evidence of this trend (Richter et al. 2005). Figure 2-1 shows the distribution of NO_2 concentrations in the troposphere of East Asia in January 1996 and 2002 (Irie et al. 2005; JAMSTEC 2005). It reveals that NO_2 concentrations are extremely high above the northern plain in eastern China and that the region of high-concentrations expanded between 1996 and 2002. Figure 2-2 shows the changes in winter concentrations (November to January) from 1996 to 2002 (difference obtained by subtracting values in 1996 from values in 2002). Areas where the increase during that period is most noticeable include Beijing, Shanghai, and Henan Province. Analysis of changes in average NO_2 concentrations by season inside the square drawn around the northern plain shows that NO_2 concentrations are highest in winter, and are increasing by eight percent per year. The same trend is evident in other seasons, with an annual rate of increase of 7 percent (±1 percent). Such increases of NO_2 concentrations in China result from increases in NOx emissions, which not only raise ozone concentrations at the ground level in China but also lead to an increase in ozone concentrations over Japan through long-distance transport of air pollution.

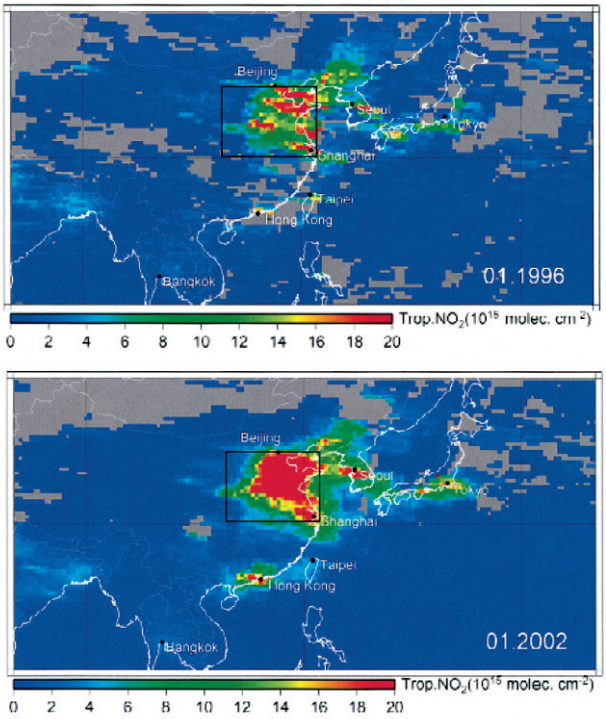

Figure 2-1. Distribution of NO_2 concentrations in the troposphere of East Asia, measured by the Global Ozone Monitoring Experiment. Shown here are average January concentrations in 1996 (top) and 2002 (bottom). Gray zones indicate lack of data. (JAMSTEC 2005)

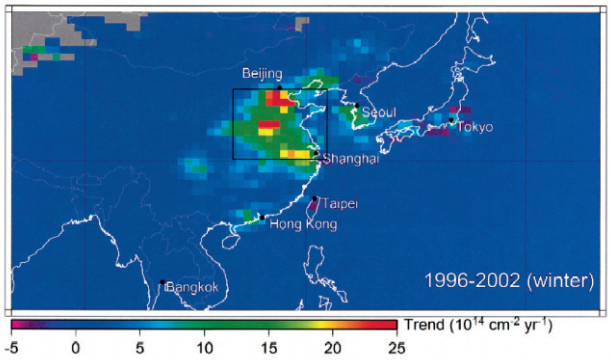

Figure 2-2. Changes in NO_2 concentrations in the troposphere in winter (November-January) between 1996 and 2002. (JAMSTEC 2005)

References

Irie, H. et al., Geophysical Research Letters, 32, L11810, 2005.

Japan Agency for Marine-Earth Science and Technology (JAMSTEC), <http://www.jamstec.go.jp/frsgc/jp/press/050617/index.html>, 2005.

Richter, A. et al., Nature, 32, 129-132, 2005.

Rising NOx and VOC emissions

In this section, we discuss trends in NOx and VOC emissions, precursors for the formation of ozone, based on estimates of emissions in Asia. Figure 2-3 shows the trend of NOx and VOC emissions in Asia, estimated by the Frontier Research Center for Global Change (FRCGC) and the Research Institute for Humanity and Nature (RIHN) (Ohara et al. 2005). NOx emissions in Asia increased by about 2.5 times over the twenty years from 1980 to 2000. China showed a dramatic increase of 3.1 times, a trend that has likely continued after 2000. Figure 2-4 compares distributions of NOx emissions in 1980 and 2000, showing that increases are large in the northern plain and the southern coastal area of China, similar to the findings of the GOME study mentioned above. Increases over Indochina and India are also dramatic. A large part of these increases in emissions is due to the rising combustion of coal in power plants and the growing popularity of the automobile.

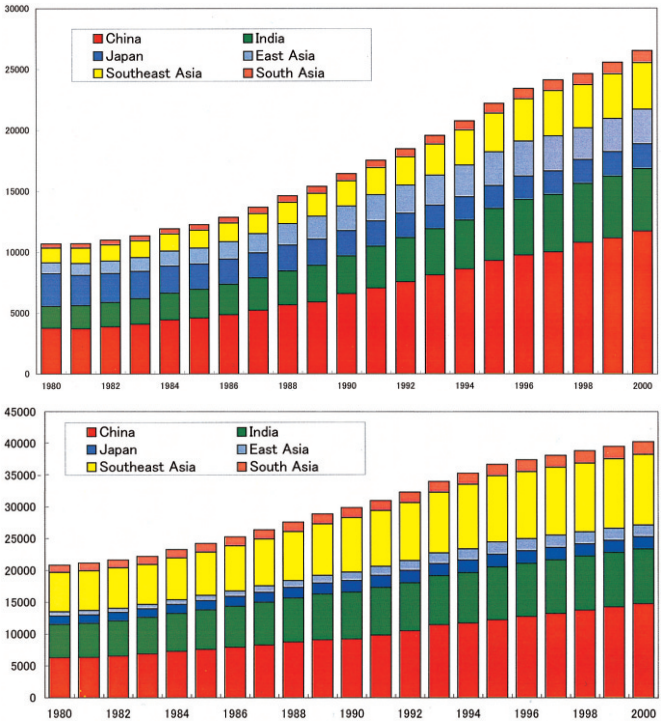

Figure 2-3. NOx (top) and VOC (bottom) emissions in Asia from 1980 to 2000. Units: Kilotons per year. (Ohara et al. 2005)

Similarly, the increase of VOC emissions is large. VOC emissions in Asia increased 1.9 times in Asia and 2.4 times in China from 1980 to 2000. The main causes of these increases are increasing emissions from automobiles and evaporation from the use of solvents.

As mentioned above, both NOx and VOC emissions, which lead to ozone formation, have been increasing dramatically in Asia over the past quarter of a century. Unless drastic measures are taken to address energy and environmental issues, NOx and VOC emissions will continue increasing. Such a scenario will mean the elevation of tropospheric ozone concentrations over a wide area, with serious consequences. Urgent action is therefore needed to reduce emissions, through international cooperation in the Asian region.

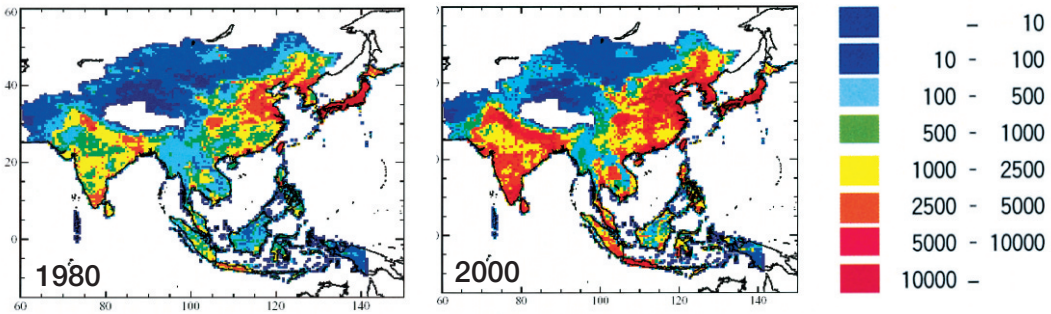

Figure 2-4. Distribution of NOx emissions in Asia in 1980 (left) and 2000 (right). Units: Tons year^{-1} per grid cell. Cells are 0.5 degrees longitude by 0.5 degrees latitude. (Ohara et al. 2005)

References

Ohara, T. et al., Proceedings of the 46th Annual Meeting of Japan Society for Atmospheric Environment (in Japanese), 511, 2005.

3. Tropospheric Ozone: A powerful Greenhouse Gas

■Greenhouse effect by ozone

Ozone has a powerful capacity to absorb infrared light with a wavelength of around 10 microns. Since these wavelengths do not overlap those of water vapor (H_2O) and carbon dioxide (CO_2), ozone in the atmosphere efficiently absorbs the infrared rays radiated from the Earth and thereby has powerful greenhouse effect. Because ozone has a relatively short lifetime in the atmosphere—from about a week to a few months, depending on the season, altitude and region—the spatial distribution of ozone is extremely uneven compared to greenhouse gases such as CO_2 that have a long lifetime. As a result, when considering the greenhouse effect caused by ozone, it is important to know how it differs depending on its location in the atmosphere.

First, let us examine the relationship between altitude and the greenhouse effect efficiency of ozone. Figure 3-1 shows the rate of change of ground-level temperature caused by increased ozone concentrations at different altitudes. As shown by the figure, the effect of warming is small at ground level. As we approach the upper troposphere, the effect becomes stronger, reaching the maximum around the tropopause, which divides the stratosphere and the troposphere, about ten kilometers above the Earth. In the lower layer of the stratosphere as well, ozone has a positive greenhouse effect. However, at an altitude above about 30 kilometers, an increase in ozone concentrations lowers the temperature at the ground level.

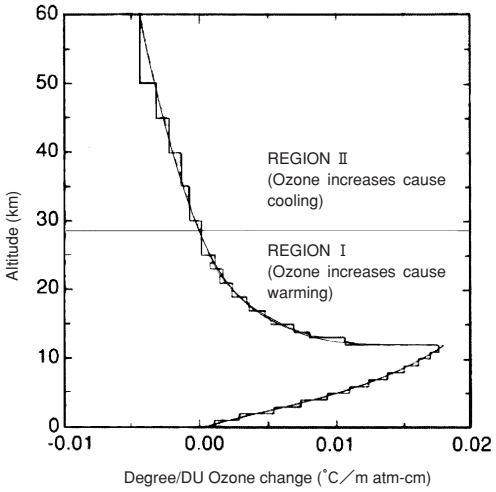

Figure 3-1. Relation between altitudes and changes of ground—level temperature caused by increase in ozone column density (DU, Dobson Units) (Based on Lacis et al. 1990)

The reason why the effect at ground level is nearly zero is that the ozone's absorption and radiation of infrared rays (from the Earth) is balanced, since the air temperature is almost the same as that of the Earth's surface and there is no net absorption. At higher altitudes, where the temperature is lower, the net of infrared absorption by ozone is larger, making the greenhouse effect more efficient. Similarly, near the tropopause where the temperature of the atmosphere is at its lowest, the greenhouse effect of ozone is at its highest. In contrast, at higher altitudes in the stratosphere where the temperature is also higher, the net absorption of infrared rays by ozone is reduced, making the greenhouse effect negative above the middle layer of the stratosphere.

In short, ozone in the troposphere and the lower layer of the stratosphere has a positive greenhouse effect. Ozone has its strongest greenhouse effect in the upper troposphere.

■Geographical distribution of global warming effect by ozone

Here, we examine the global distribution of the effects of ozone on global warming. Figure 3-2 is a scenario simulated by a chemical-climate model showing the global distribution of the effects of tropospheric ozone concentrations that increased between the Industrial Revolution and 1990. It shows that the effects on global warming are the largest in the southern region of the Mediterranean Sea, the northern part of Africa and the Middle East. These are followed by the southern parts of North America and Europe and the southeastern part of Asia. The effects of tropospheric ozone on global warming extend to Japan as well, from the main island of Honshu southwards. The reason why the regions feeling the greatest effects are shifted south from the areas where ozone is highest in concentration (Figures 1-1 and 1-3) is that greenhouse effect of ozone is largest in the regions with more solar radiation and fewer clouds.

Since the increase of tropospheric ozone in the northern hemisphere is larger than in the southern hemisphere due to the higher intensity of human activities in the North, in the past the global warming effects of ozone have been much greater in the northern hemisphere. In addition, even within the northern hemisphere, there are large differences in the size of the effects depending on location. These are special features of the greenhouse effect of tropospheric ozone.

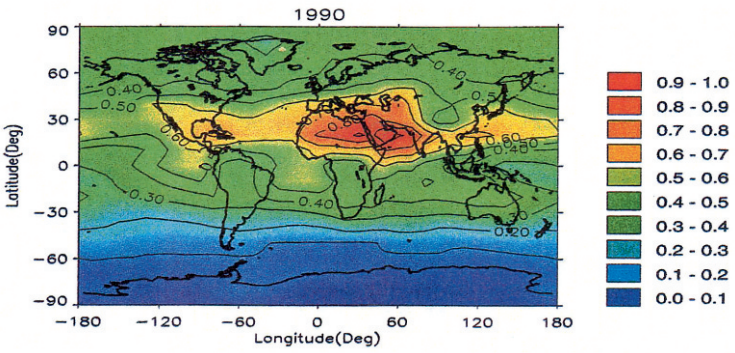

Figure 3-2. Annual average climate forcings in 1990 caused by the increase of tropospheric ozone since 1850, with normalized relative values by annual average maximum value in 1990. (Bernsten et al. 2000)

Ozone, the third most powerful greenhouse gas

We have shown that the greenhouse effect of ozone differs largely by region. In this section, we compare the average global warming effect of ozone on the entire Earth with those of other greenhouse gases. For the purpose of comparing effects on global warming, an indicator called climate forcing is generally used. This index (in Watts per square meter, or W/m^2) is obtained by assessing to what extent infrared light passing through the tropopause is reduced as the concentration of a given greenhouse gas increases in the atmosphere. Figure 3-3 describes the effects on global warming that several kinds of greenhouse gases have caused since immediately before the Industrial Revolution to the present. CO_2 has had the largest effect on global warming, followed by methane and tropospheric ozone. This is why the IPCC calls tropospheric ozone "the third greenhouse gas." It should be noted that the figure compares the average global warming effects on the entire planet. As shown above, the increase of tropospheric ozone in the northern hemisphere is larger than in the southern hemisphere, and the past effects on global warming are also much larger in the northern hemisphere. In addition, because of the localization of effects even in the northern hemisphere, the effects of ozone on global warming may be much larger in some regions than in others. Figure 3-3 also shows that the climate forcings of aerosols, which like ozone are also air pollutants with short lifetimes, are very large (both positive and negative), and differ greatly depending on the chemical components.

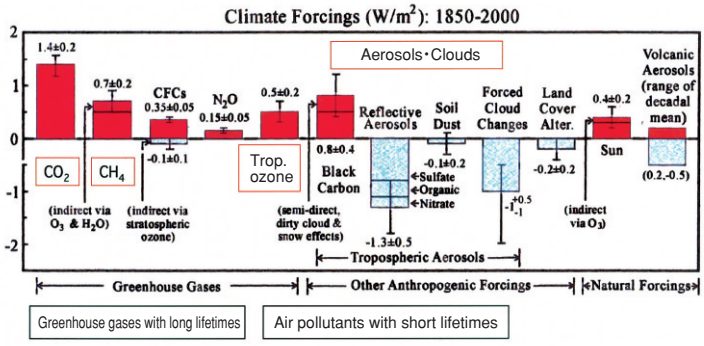

Figure 3-3. Global climate forcings of different greenhouse gases from 1850 to 2000. (Based on Hansen and Sato 2001)

References

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4. New Concerns about Health Effects of Ozone

■Health effects of ozone

"Photochemical oxidants" are substances such as ozone and peroxyacetylnitrate (PAN), formed secondarily through photochemical reactions. They cause what is known as photochemical smog. Approximately 90 percent of the components are ozone (O_3), which is the main cause for the health effects of photochemical oxidants. Since ozone is not very soluble in water, if ozone is inhaled, it goes through the trachea unabsorbed before going deeply into the lungs and reaching the alveoli. The strong oxidizing action causes a variety of damage to living cells. Most common symptoms are acute effects, including stinging of the eyes, tears, sore throat and coughing, due to irritation of the mucous membranes of eyes, nose and throat.

In animal experiments, with concentrations more than about 0.12 ppm, type I alveoli cells are destroyed quickly, while type II cells, alveolar macrophages and polynuclear white blood cells increase. Next, cilia drop out or disappear. As a result, hypertrophy of the epidermis is observed in the bronchial tube and alveolar walls. As for biochemical changes, it is reported that, due to oxidation stress, products from the decomposition of lipid peroxide increase and the anti-oxidation activity of enzymes is amplified. With regard to changes of respiratory functions, at concentrations of 0.3 to 0.4 ppm or higher, studies have reported increases of tracheal resistance, decreases of dynamic lung compliance, and, in guinea pigs exposed to low concentrations for long periods, hypersensitiveness of the trachea. In human asthmatics exposed to concentrations of 0.08 ppm or higher the forced expiratory volume (FEV) is reduced during physical exercise.

■Collective health damage from photochemical oxidants in Japan

In 1970 for the first time in Japan, a group of people suffered negative health impacts apparently caused by photochemical oxidants. The incident took place at a senior high school in the Suginami Ward of Tokyo. Female students exercising in the schoolyard and people living in the neighborhood complained of stinging eyes and throats as well as other non-respiratory symptoms like nausea, dizziness and fainting. Some students were hospitalized.

Respiratory impacts had been considered the main health effects of air pollutants before that incident. The atmospheric ozone concentrations at that time were estimated to be about 0.2 ppm—not considered to be high enough to cause acute respiratory symptoms. The mechanisms causing neurological symptoms like nausea and dizziness are not entirely clear. However, subsequent animal experiments suggested that they could be caused by ozone stimulation leading to irritation of parasympathetic nerves, and suppression of sympathetic nerves, which cause decreases in heart rate and blood pressure, and irregular pulse (Figure 4-1).

As a result of such incidents of negative health impacts, the government established an air quality standard for photochemical oxidants in 1973. Unlike the other air pollutants, it was set at a level to prevent acute rather than chronic effects, at 0.06 ppm or lower as an hourly value.

■Attainment of environmental standards, complaints of health damage

In 2004, the attainment rate of the air quality standard for photochemical oxidants was extremely low in Japan. Only two stations attained the daytime standard (5 a.m. to 8 p.m.) and never exceeded the hourly maximum of 0.12 ppm. This represents only 0.2 percent of all the stations in Japan, including ambient and roadside monitoring stations. Although the total number of days having photochemical oxidant warnings had been decreasing since a peak in 1973, this number has been fluctuating since the 1980s. In 2004, photochemical oxidant warnings were issued in 22

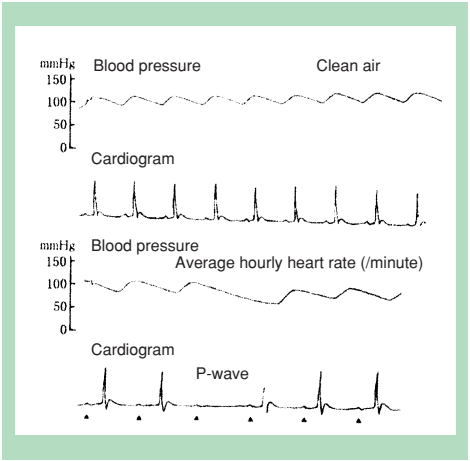

Figure 4-1. Blood pressure decrease and irregular pulse in rats exposed to 1 ppm-ozone for three hours. (Uchiyama 2003)

prefectures, with a cumulative total 189 days of warnings in all prefectures, and 393 reported victims apparently affected by photochemical oxidants.

Although incidences of health impacts are less common than in the past, they are still reported periodically. Once a photochemical oxidant warning is issued, people are advised to avoid outdoor exercise, and any physical education being conducted outdoors at schools must be moved indoors.

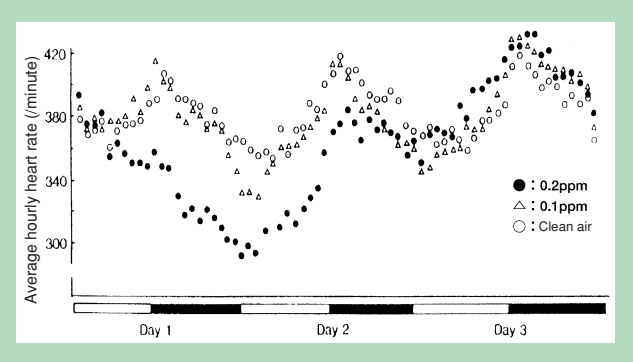

Figure 4-2. Changes in heart rate when exposed to ozone for three consecutive days. (Arito et al. 1990)

Under repeated ozone exposure, reactions such as the decline of respiratory functions in humans and decreased heart rate in animal experiments are most evident on the first day, but in about three days, they no longer occur under the same atmospheric concentrations (Figure 4-2). Likewise, health damage caused by photochemical oxidants is more likely to occur when the concentration of oxidants rises suddenly, for example, on a sunny day in Japan's rainy season, rather than when the concentration of oxidants has risen gradually with a series of hot days in midsummer.

People sometimes complain or question the need to change their behavior after an warning is issued, for example when they are told they must stop swimming in an outdoor pool. However, it is important to follow the actions required when warnings are issued, as high oxidant levels may induce the acute symptoms mentioned above, as well as other impacts such as asthma attacks in children suffering from asthma.

Standards in Europe and the United States

The United States Environmental Protection Agency (USEPA), during a standards review process in 1996, considered that (1) even with hourly concentrations of 0.12 ppm or lower, acute health effects can be observed if people are exposed to ozone for a long period while doing a medium level of exercise; (2) pulmonary damage observed as chronic effects in animal experiments with ozone are almost the same regardless of species; and (3) repeated inflammation by ozone exposure during life may damage pulmonary tissues and reduce the quality of life in old age. Since most regions in the United States had attained existing standards for hourly concentrations, the USEPA felt that an eight-hour value would now be more appropriate than a one-hour value, for properly controlling exposure levels and preventing harmful effects. Thus, an eight-hour mean value of 0.08 ppm was judged as appropriate, based on risk assessments, especially on the proportion of children who suffer from medium or high level decline in pulmonary functions through outdoor activities, and the proportion of children who experience chest pains when breathing deeply.

In the United Kingdom, the provisional target of ozone concentrations to be achieved by the end of 2005 was set at 100μg/m^3 (0.05 ppm) as a daily maximum running eight-hour mean not to be exceeded more than ten times a year. Similarly, the European Union set the eight-hour value (calculated four times a day) of 110μg/m^3 (0.055ppm) as a target to be achieved by 2010. Both were established as a permissible range of concentrations, from the public health perspective, based on risk assessments of health effects such as aggravation of symptoms and respiratory functions of asthmatics and the increased hospitalization of patients with respiratory disease. Other thresholds, such as a yearly mean value, have not yet been established, however, since chronic effects have not yet been adequately determined in epidemiological studies.

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5. Ozone Damage to Agricultural Crops

■Discoveries of ozone damage in plants

In 1944, photochemical smog damage was observed for the first time on plants near Los Angeles in the United States. Later, ozone was identified as the primary causal agent of the damage. Since then, many studies conducted on the effects of ozone on plants have shown that ozone is damaging plants in various regions across Japan, Europe and North America. When a high-concentration of ozone diffuses into a plant, the strong oxidizing power injures the plant tissues, resulting in visible damage, such as white, yellow, or reddish spots in the leaves. The leaf damage in leafy vegetables like spinach reduces the commercial value significantly (Photo 5-1). Even if the ozone concentration is less than a level that causes visible damage, the elevated level of ozone concentrations reduces the photosynthesis function and accelerates aging in plant leaves. Plant growth is hence retarded, and, in agricultural crops, the harvest is reduced.

Photo 5-1. Ozone damage to spinach leaves. (Photo courtesy by Dr. Isamu Nouchi, National Institute for Agro-Environmental Sciences)

■Agricultural production losses caused by ozone

To estimate the amount of crop harvest lost to ozone, researchers have studied crop plants grown in greenhouses where ozone concentrations were raised compared to the ambient air. The observed changes in the crop yield were related to average ozone concentrations during the daytime for major crop species (Figure 5-1). The relationships for corn, winter wheat, cotton and soybean have been derived from the experiments in the United States (Lesser et al. 1990), for spring wheat from experiments in Europe (Skärby et al. 1993), and for rice from an experiment in Japan (Kobayashi et al. 1995). The relationship between ozone and yield loss differs with crop species: rice, corn and winter wheat are less sensitive to ozone than cotton and soybean, whereas spring wheat in Europe is, interestingly, as sensitive as soybean in the United States. In addition, even the same species can show different sensitivity among different varieties and under different environments. Therefore, it would be more realistic to consider the relationships in Figure 5-1 as a collection of wide bands rather than as lines. We do not yet know exactly how the width of the bands is determined, however.

Using the relationships shown in Figure 5-1, crop yield losses due to ozone were estimated for soybean and winter wheat across the United States, except for the middle and western regions. The result showed a 14 percent loss on average over the six years from 1982 to 1987 (Tingey et al. 1994). As for Japanese rice, the yield loss in the Kanto region was estimated to be around three percent on average over the five years from 1981 to 1985 with the highest loss of up to seven percent in the middle of the region (Figure 5-2). Takagi and Ohara (2003) also estimated a yield loss of rice about 3.5 percent in the Kanto region using more recent data of ozone from 1996.

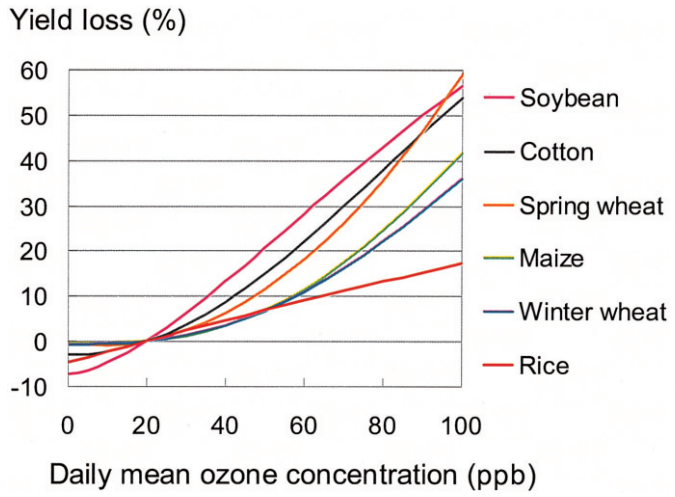

Figure 5-1. Relationships between ozone concentrations and yield losses in major agricultural crops. (Lesser et al. 1990; Skärby et al. 1993; Kobayashi et al. 1995)

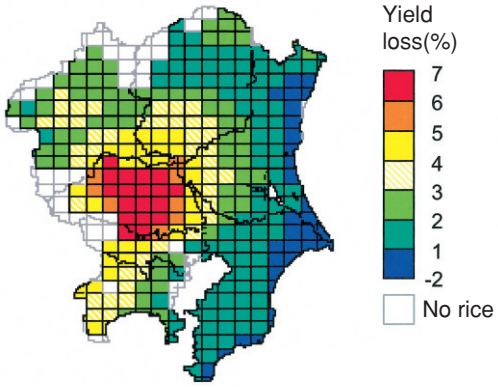

Figure 5-2. Yield loss of rice caused by ozone in the Kanto region of Japan. Relative yield loss (%) was compared to yields at a reference ozone concentration (20 ppb), and averaged over five years from 1981 to 1985. (Kobayashi 1999)

Rising impacts of ozone across Asia

As in other industrialized regions of the world, surface ozone concentrations are increasing in Asia, and their impacts on agricultural crops and natural vegetation have become a matter of concern among scientists. Wang et al. (2005) estimated that the yield of winter wheat was reduced by about 25 percent in the lower Yangtze River basin in 2000, with the mean daytime ozone concentration from April to June being around 60 ppb. For rice, Wang et al. (2005) estimated the average daytime ozone concentration to be 45 to 50 ppb during the growing season (June to October). The yield loss of rice could therefore be about seven percent using the relationship shown in Figure 5-1. With rapid economic growth occurring in China, there is strong reason to expect further increases in ozone concentrations in the future. Wang and Mauzerall (2004) predicted that daytime surface ozone concentrations in July will exceed 55 ppb in most parts of China in 2020, using a global-scale model of atmospheric chemistry and transport. They also predicted that the total production of soybean, corn and winter wheat in China will be reduced by about 40 to 60 percent in 2020. Since Chinese crop production is the world's largest for wheat, second-largest for corn, and fourth-largest for soybean, the Wang-Mauzerall predictions on the crop losses to ozone have very strong implications for the global food supply in the future. Admittedly, there are many uncertainties in their predictions, and future studies may lead to more moderate estimates of crop losses. Nevertheless, considering that we now have less than 15 years remaining before 2020, and that the implications of ozone impacts are so significant, it will be important to launch further studies as soon as possible to minimize the uncertainties in crop loss predictions.

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6. Ozone Threat to Japan's Forests

■Tree damage in Japan

Forests act as a life-support system on the Earth. Through photosynthesis, trees, a main component of forest ecosystems, supply the oxygen that is indispensable to support life. Forests also preserve our environment by fixing carbon dioxide, a major cause of the global warming, and by absorbing air pollutants. Unfortunately, forest decline and tree dieback are being observed in many areas of Japan (Izuta 2001).

In the Tanzawa Mountains of Kanagawa Prefecture, the decline and dieback of Japanese beech (*Fagus crenata*) have been observed at Mt. Hinokiboramaru and Mt. Hirugatake (Photo 6-1 top), and decline of Japanese fir (*Abies firma*) has been observed at Mt. Ohyama. In the Oku-Nikko area of Tochigi Prefecture, Veitch's fir (*Abies veitchii*), Maries fir (*Abies mariesii*) and Erman's birch (*Betula ermanii*) are in a state of decline (Photo 6-1 bottom). In the Sanyo Region, which includes Hiroshima Prefecture, the decline of Japanese red pine (*Pinus densiflora*) has been observed. In some areas along the Sea of Japan, including Ishikawa, Tottori and Shimane Prefectures, the decline and dieback of konara oak (*Quercus serrata*) and mizunara oak (*Quercus mongolica*) have also been observed.

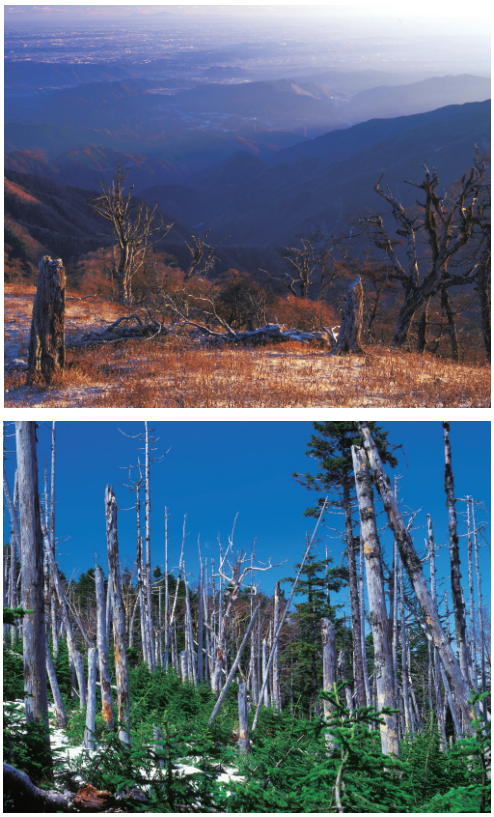

Photo 6-1. Decline of Japanese beech at Mt. Hirugatake, Kanagawa Prefecture in 1995 (top photo). Veitch's fir and Maries fir in Oku-Nikko, Tochigi Prefecture in 1994 (bottom photo). Photos: Dr. Yoshihisa Kohno.

■Suspected causes of forest damage elsewhere

Several hypotheses have been presented on the causes of forest decline or tree dieback in Europe and North America. Possible causes differ with each site. Ozone, soil acidification due to acid deposition and excess nitrogen deposition from the atmosphere have been suggested as causes in northern Europe; ozone, acid deposition such as acid mist and fog and sulfur dioxide have been suggested in western Europe; and sulfur dioxide, nitrogen dioxide, ozone and acid deposition such as acid mist/fog have been suggested in eastern Europe. In North America, meanwhile, ozone is thought to be closely related to the forest decline and tree dieback. For example, in the Sierra Nevada-San Bernardino Mountains, ozone is regarded as the main cause of the decline of pine species such as ponderosa pine (*Pinus ponderosa*) and Jeffrey Pine (*Pinus jeffreyi*). In the northern Appalachian Mountains, where the decline of red spruce (*Picea rubens*) has been observed, relatively high concentrations of ozone have been recorded. In the southeastern part of the United States, it has also been suggested that ozone is a factor in the decline of eastern white pine (*Pinus strobus*).

In Japan, tropospheric ozone concentrations have been increasing in recent years, and concentrations of ozone high enough to cause harmful effects on forest tree species have been recorded. Based on these facts, ozone is considered to be one of the main factors relating to forest decline and tree dieback in Japan. In fact, relatively high concentrations of ozone over 100 ppb have been recorded in the Oku-Nikko area and at Mt. Hinokiboramaru in the Tanzawa Mountains, where the decline and dieback of Japanese beech (*Fagus crenata*) have been observed. Thus, adverse impacts of ambient ozone on growth and physiological functions such as photosynthesis of forest tree species are matters of concern.

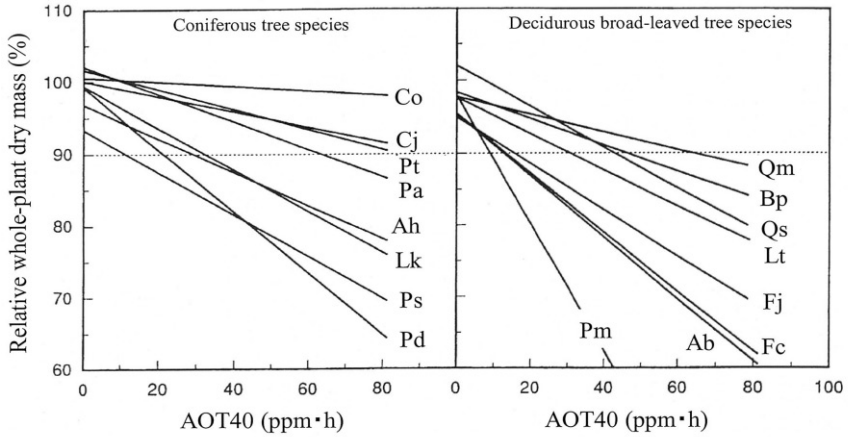

Figure 6-1. Relationship between the whole-plant dry mass forest tree species and AOT40 of ozone (Izuta and Matsumura 1997). The horizontal axis shows AOT40 of ozone calculated for six months, and the vertical axis indicates relative value of the whole-plant dry mass of the seedlings exposed to ozone to that of the seedlings exposed to charcoal-filtered air.

Legend for species: Pd, *Pinus densiflora* (Japanese red pine); Pt, *Pinus thunbergii* (Japanese black pine); Ps, *Pinus strobus* (eastern white pine); Lk, *Larix kaempferi* (Japanese larch); Pa, *Picea abies* (Norway spruce); Ah, *Abies homolepis* (Nikko fir); Co, *Chamaecyparis obtusa* (Japanese cypress); Cj, *Cryptomeria japonica* (Japanese cedar); Pm, *Populus maximowiczii* (Japanese poplar); Bp, *Betula platyphylla* (Japanese white birch); Qs, *Quercus serrata* (konara oak); Qm, *Quercus mongolica* (mizunara oak); Fc, *Fagus crenata* (Japanese beech); Lt, *Liriodendron tulipifera* (yellow poplar); Ab, *Acer buergerianum* (trident maple); Fj, *Fraxinus japonica* (Japanese ash).

Effects of ozone on Japanese tree species

Ozone in the atmosphere is absorbed into the leaf tissues of trees through the stomata, and causes visible damage on the leaves, as well as a reduction of growth and suppression of physiological functions such as photosynthesis. Based on the results obtained from several studies conducted in Japan, there are great differences in ozone sensitivity among Japanese forest tree species, in terms of growth and net photosynthesis. To clarify the sensitivity of growth of forest tree species to ozone, in one study, seedlings of 16 tree species were exposed to either charcoal-filtered air or ozone for several years (Figure 6-1). The study ranked various species for ozone sensitivity of the whole-plant dry mass with accumulated ozone exposure over a threshold of 40 ppb (AOT40; see page 17 for details) at 20 ppm･h [from high to low sensitivity: Japanese poplar (*Populus maximowiczii*) > trident maple (*Acer buergerianum*) > Japanese beech (*Fagus crenata*) and eastern white pine (*Pinus strobus*) > Japanese ash (*Fraxinus japonica*) > Japanese red pine (*Pinus densiflora*) > Nikko fir (*Abies homolepis*) > yellow poplar (*Liriodendron tulipifera*) > Japanese larch (*Larix kaempferi*) > Japanese white birch (*Betula platyphylla* var. japonica) and mizunara oak (*Quercus mongolica*) > konara oak (*Quercus serrata*) > Japanese cedar (*Cryptomeria japonica*) and Norway spruce (*Picea abies*) > Japanese black pine (*Pinus thunbergii*) > Japanese cypress (*Chamaecyparis obtuse*)]. The AOT40 values corresponding to a 10 percent reduction in the whole-plant dry mass were approximately 8 ppm･h for Japanese popular, the most sensitive species, and 12-21 ppm･h for Japanese red pine, eastern white pine, Japanese beech, trident maple and Japanese ash.

In Maebashi City of Gunma Prefecture, the site of the study described above, AOT40 values for six months were 10-24 ppm･h. At Inukoeji in the Tanzawa Mountains of Kanagawa Prefecture, relatively high concentrations of ozone over 0.12 ppm were observed, and the AOT40 value from March to June in 1997 was approximately 30 ppm･h (Aso 1999). Taking these observations and results of experimental studies into account, it can be deduced that ozone causes harmful effects on relatively sensitive tree species such as Japanese beech. Since tropospheric ozone concentrations are expected to increase steadily in Japan, ozone has the potential to adversely affect many Japanese forest tree species in the future.

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7. Environmental Standards and Other Indexes for Ozone Exposure

Terms such as "standards" and "criteria" are commonly used to describe indicators. The World Health Organization (WHO) uses the term "guidelines." The values of environmental standards for air pollutants are expressed in terms of "concentrations" or "doses." Several expressions are used as units of measure for concentrations, such as hourly average, daily average, daily maximum of hourly values, monthly average, annual average. The environmental standard of photochemical oxidants in Japan is stated, for example, as the "one-hour value must be 0.06 ppm or lower." Units of dose such as "ppm·h" express concentrations multiplied by time. The same concentration will result in a different dose if the period of exposure is different. Conversely, it is important to note that, for example, a 20-hour exposure to 0.05 ppm amounts to the same 1 ppm·h dose that would result from a 1-hour exposure to 1 ppm. Even if the dose is the same, long-term exposure to low concentrations, or short-term exposure to high concentrations, may cause different reactions in organisms. These examples show that actual exposure conditions should be fully considered when evaluating the results of experiments.

Standards in concentration or dose are decided based on reviews of the latest scientific knowledge from monitoring results, epidemiological studies, and exposure experiments for human beings, animals, and plants. Since the methods of setting standards differ with each country, region, and affected subject, no common standard is used worldwide (see table on pages 25 and 26).

■Standards for plants (crops, forests, and ecosystems, etc.)

In general, national environmental standards are set mainly for the protection of human health in each country, and most of them are based on concentrations. However, European and other countries have begun to apply the concept of "critical levels" that incorporate the idea of doses.

A critical level is defined as "the concentrations of pollutants in the atmosphere above which direct adverse effects on receptors (such as human beings, plants, ecosystems or materials) may occur, based on current knowledge." A related term, "critical load," is defined as "a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur, based on current knowledge."

■AOT40 and SUM60

Europe originally used concentration-based standards for ozone, but it has been replaced by a new index called AOT40, which refers to cumulative ozone exposure above a threshold of 40 ppb (Fuhrer et al. 1997) (Figure 7-1). By definition, AOT40 drops to zero when ozone concentrations stay below 40 ppb for a certain period.

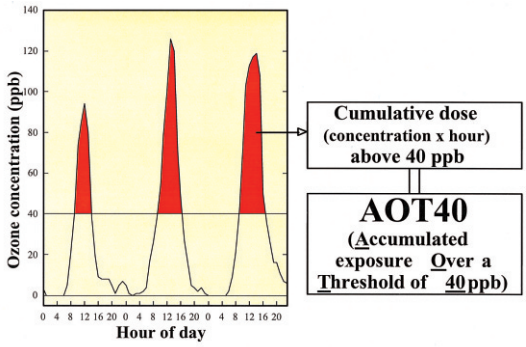

Figure 7-1. Calculation of AOT40. (Redrawn from Fuhrer et al. 1997)
Cumulative dose over 40 ppb (concentration × time)

In Europe, 3 ppm·h has been proposed as the AOT40 for three months corresponding to a 5 percent yield reduction of crops, based on open-top chamber experiments with wheat cultivars for 10 growing seasons in six countries. The AOT40 of 3 ppm·h was also suggested as the critical level (Level I standard) for 10 percent growth reduction on grassland and pasture (natural and semi-natural vegetation). As for forests, the AOT40 of 10 ppm·h was suggested as the critical level (Level I standard) for 10 percent growth reduction based on experiments of ozone exposure to beech trees. Since growth conditions, such as temperature and soil moisture, have not been reflected in those critical levels, discussions on Level II critical levels were necessary to consider effects of those factors. In this context,

discussions were started on flux-based critical levels, with the result that a flux threshold of 1.6 nmol/m^2/s (about 0.077μg/m^2/s) was proposed as a preliminary value for forests (Karlsson et al. 2003).

While European countries discuss the AOT40 as the critical level of ozone, the United States and Canada are discussing another index, known as SUM60. This is the sum of hourly ozone concentrations equal to or greater than 60 ppb over a given period. As with AOT40, "ppm･h" is also used as the units for SUM60. While the AOT40 is the sum of the differences between hourly ozone concentrations and 40 ppb for each hour, SUM60 is the sum of concentrations that exceed 60 ppb.

Mapping of areas exceeding critical levels

Mapping of monitoring data on the atmosphere in relation to those critical levels makes it possible to study where the ozone concentrations exceed the critical level, to what extent, and which areas have high risk of ozone effects. Yield of agricultural crops can also be evaluated and discussed based on the mapping. Figure 7-2 is a map available on the Internet showing the spatial distribution of SUM60 in the United States.

In Japan, estimates were also made in recent years regarding the effects on rice yield and growth, but the area studied was limited to the Kanto region (Takagi and Ohara 2003; Yonekura et al. 2005).

Japan's nation-wide monitoring system observes photochemical oxidants, rather than ozone concentrations. Published data include the number of hours when concentrations exceed 0.06 ppm and exceed 0.12 ppm at each monitoring station, only during the daytime, so 24-hour statistical data are not available except for limited sites. Thus, in one study, the AOT40s at each station were estimated in detail based on the relationship between the number of hours exceeding the standards and hourly concentrations. This analysis showed that the AOT40 in Japan was approximately 5 ppm･h in the early 1980s, then gradually increased year by year, to the point that it exceeded 10 ppm･h after the year 2000 (Figure 7-3). Analysis on the nation-wide spatial distribution shows that the AOT40 is high in suburban areas of large cities, for example, in the Kanto region, Osaka, and Hiroshima. In the Kanto region, the AOT40 is extremely high in Saitama and Gunma Prefectures (Figure 7-4).

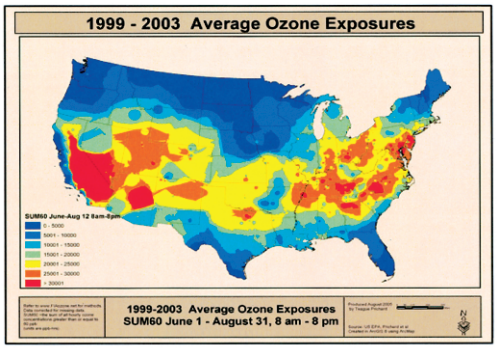

Figure 7-2. Five-year average (1999-2003) of ambient ozone exposures using SUM60 in the United States. (USFS-FIA)
Period: June 1-August 31
Time: 8 a.m.-8 p.m.
Contour lines: Increments of 5 ppm･h. (Area near California exceeds 30 ppm･h.)

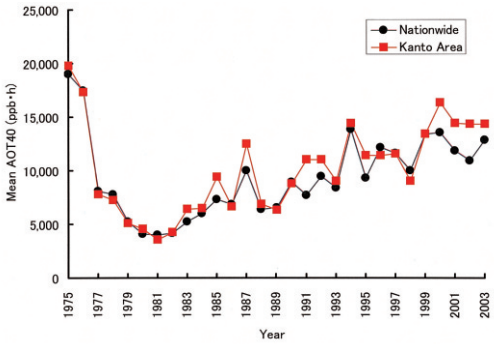

Figure 7-3. Trend of mean AOT40 for photochemical oxidants (Ox) in Japan. AOT40 was estimated by calculating from sum of numbers of hours exceeding 0.06 and 0.12 ppm. (Kohno 2005)

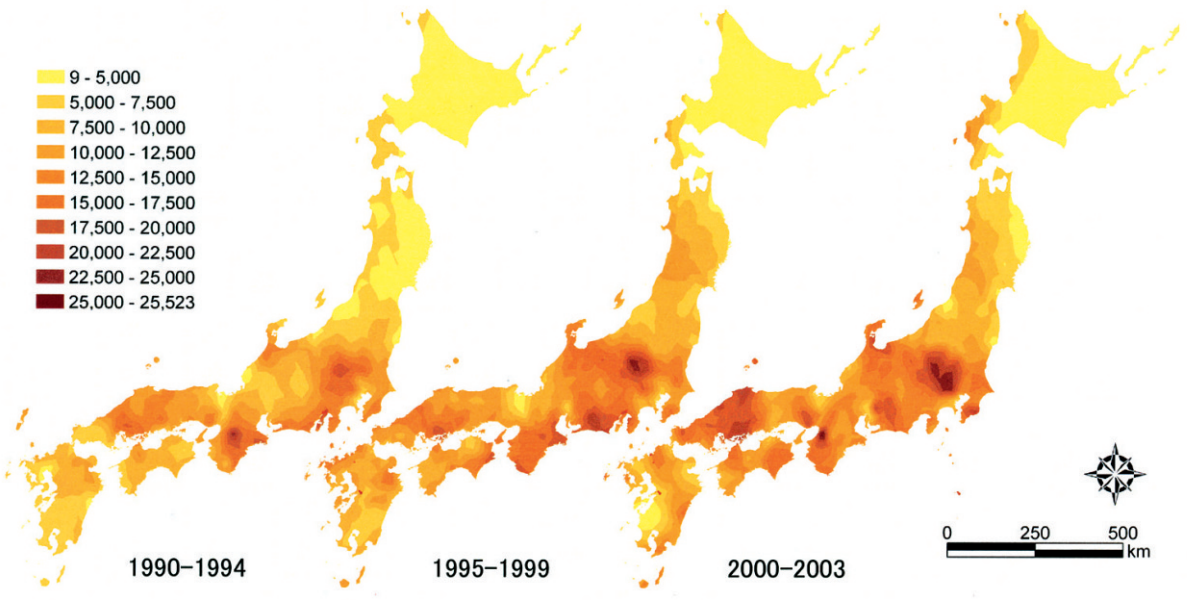

Figure 7-4. Mean AOT40 for photochemical oxidants (Ox) in Japan.
AOT40 was estimated and mapped by calculating from sum of numbers of hours exceeding 0.06 and 0.12 ppm. Units: ppb･h. (Kohno 2005)

Monitoring stations for ozone and oxidants of Japan are located mainly in densely populated urban areas, and only a few stations are in mountainous areas. For the conservation of the natural environment, it will be important to take measures to strengthen monitoring in such areas that now provide insufficient data. When we consider that, except for Japan, stations equipped with automatic ozone monitors are very limited in number in East Asia, it is clear that this region is far behind Europe and North America in monitoring and research systems on ozone and oxidants.

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8. The Ozone Threat in East Asia

Models of growing ozone pollution in East Asia

The first chapter showed that tropospheric ozone concentrations are increasing in the northern hemisphere in large regions of intense human activity. In this chapter, we examine the situation of ozone pollution in East Asia. While the current status is not necessarily clear, due to the lack of an extensive monitoring network on the ground, recent developments in modeling enable relatively accurate descriptions of the geographical distribution of ozone pollution.

Figure 8-1 is the result of a regional-scale chemical transport model, showing the distribution of monthly average ozone concentrations from spring to summer in East Asia.

The figure reveals high ground-level ozone concentrations in spring and summer in large parts of East Asia, and a band of high-concentration ozone extending from Central Asia to the Pacific Ocean. The concentrations reached a peak in May in Japan, and in June in the middle of the Asian continent. The peak in June is thought to be due to the highest intensity of ultraviolet light from the sun in that month. Japan's peak in May, rather than June, is thought to be due to the fact that June is generally the rainy season there. Although July and August are the months when high ozone concentrations are most likely to occur in major cities in Japan, the average concentration all over Japan in summer is lower than the period from spring to early summer, due to the influences of the monsoon resulting from high atmospheric pressure over the Pacific Ocean. In the figure, the worst ozone pollution, with a monthly average of more than 70 ppb, appears to occur in the eastern region of the Asian continent where the emissions of air pollutants may be the highest in East Asia.

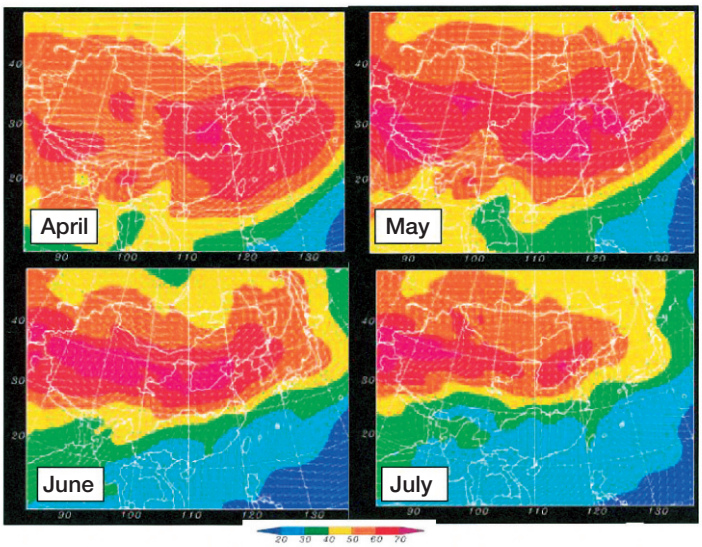

Figure 8-1. Ozone distribution at the ground level in East Asia in the spring and summer of 1996. Calculated by a regional-scale model with 80 km resolution. Dark red and light red indicate more than 70 and 60 ppb, respectively (monthly average). Orange and yellow indicate more than 50 and 40 ppb, respectively. (Zhu et al. 2005)

Evidence of the threat of ozone pollution in East Asia

What are the impacts on Japan caused by ozone pollution covering all of East Asia? The results of monitoring on the Oki islands in the Sea of Japan, may be a useful illustration of the impacts on Japan of ozone from the continent. Figure 8-2 shows the variation of ozone concentrations (hourly values) at the Oki monitoring station of the Acid Deposition Monitoring Network in East Asia (EANET) (see page 24) in May 1994.

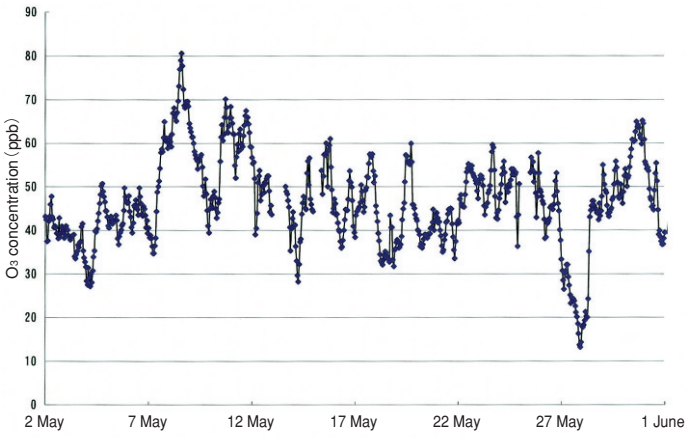

Figure 8-2. Hourly values of ozone concentrations monitored on Oki islands (Sea of Japan) in May 1994. (Akimoto 2003)

Pollutants emitted from Japan have almost no impact at this remote site, so one can assume that the Asian continent is the source. Ozone concentrations often exceeded the Japanese environmental standard of 60 ppb, and peaked at 80 ppb.

Figure 8-3 classifies the ozone concentrations monitored in Oki by type of air mass, in an effort to clarify the influence of the long-range transport of pollutants. As shown by the graph, ozone concentrations were highest in air masses indicated by black square (■), which had passed through regions of intensive human activity on the Asian continent; they were lowest in air masses indicated by white circles (○), which came directly from Siberia (also part of the Asian continent). The ozone concentrations of the former air mass reached 55 ppb (monthly average) from spring to autumn. The difference of concentrations between the air masses shown by ■ and ○ is thought to represent the influence of ozone produced on the Asian continent and transported to Japan. It is about 20 ppb (monthly average) in summer and 10 to 15 ppb in spring and autumn, as shown.

Emissions of pollutants are likely to increase with future economic development in East Asia. If that increase contributes 10 ppb to ozone concentrations in Japan, even remote or rural areas in Japan will be exposed to ozone concentrations exceeding 60 ppb during spring and summer. Concentrations of photochemical oxidants in major cities will also rise further and result in more days exceeding thresholds that trigger pollution warnings. This model also suggests that China and Korea will also experience increasingly serious environmental impacts from ozone pollution.

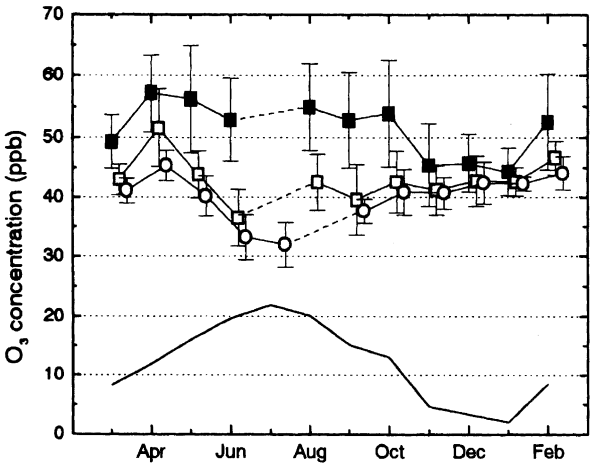

Figure 8-3. Ozone concentrations (monthly averages) on Oki islands (Sea of Japan), monitored in the air masses from the Asian continent in 1994 and 1995.

■ Polluted air mass that passed over areas of intense human activity in East Asia

○ Relatively clean continental air mass from Siberia (did not pass through polluted areas in East Asia)

Solid line at bottom indicates the difference in ozone concentrations between the polluted air masses and clean air masses. (Pochanart et al. 1999)

References

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Pochanart, P. et al., Journal of Geophysical Research, 104, 3621-3631, 1999.
Zhu, B. et al., Geophysical Research Letters, 31, L17104, 2004.

9. Future Research and Monitoring Needs

Past observations and experiments and recently-developed atmospheric chemistry models have revealed the impacts on human health and plants caused by tropospheric ozone, an air pollutant formed by reactions involving nitrogen oxides (NOx) and volatile organic compounds (VOCs).

Ozone concentrations are particularly high in the middle and high latitudes of the northern hemisphere, where the background ozone concentrations have more than doubled during the last century. In Japan as well, ozone concentrations have been increasing across the country.

Emissions of ozone precursors have more than doubled (for NOx) or doubled (for VOCs) in Asia over the twenty years from 1980 to 2000. NOx concentrations are particularly high in China's northern plain, where they continue to increase by about 7 percent per year. Tropospheric ozone is also a strong greenhouse gas, considered to be the third most important after carbon dioxide and methane.

Ozone is known to have negative effects on human health, such as on respiratory functions. Paying special attention to the health effects of long-term ozone exposure, countries of Europe and North America have established environmental standards of eight-hour value to protect human health. As for the effects of ozone on vegetation, it is thought that sensitive species such as the beech tree have already been negatively affected in Japan, and that other species will also be affected in the coming years. As crop yields are also reduced by ozone exposure, crop production in 2020 is expected to see further declines due to increases in ozone concentrations around the world.

Factors that have contributed to the increased photochemical oxidant concentrations in Japan include changes in climatic variables such as temperature and solar radiation, changes in the ratio of NOx to VOCs in the atmosphere, and increased transboundary air pollution. Long-term increases in background ozone levels suggest that tropospheric ozone has become a major issue affecting not only all of East Asia, but also the entire northern hemisphere.

■Future research needs

As mentioned above, tropospheric ozone has become increasingly important as a form of transboundary air pollution. In order to properly address this problem, further studies are needed in the following areas.

Monitoring and data analysis

At EANET monitoring sites in East Asia, continuous measurements of ozone, NOx, and VOCs, should be given a higher priority, and an effort should be made to introduce well-calibrated instruments. Information technology should be exploited further for data acquisition and distribution via the Internet.

To verify the intercontinental transport of pollutants, it is also important to consider the expansion of monitoring networks to include South and Central Asia, and the Middle East. Efforts should also be made to establish the capacity for satellite-based monitoring of air pollution in Asia.

Emission inventories

To provide information for modeling and to consider measures for rational reduction, it is necessary to prepare and improve emission inventories of both anthropogenic and natural sources of NOx and VOCs, the precursors of ozone in the atmosphere. (An emission inventory is a list of emission sources and amounts in a nation or a region, etc.) Systems for sharing, publishing, reporting, utilizing and updating these inventories should also be established.

Modeling

The accuracy of projections in models should be enhanced through greater sophistication of models dealing with the transport, diffusion, reactions and deposition processes related to ozone, and verification using monitoring data. It is also important to create integrated models dealing with different scales, from the city to the global scale, which will allow estimations of interactions between large and small scales. It is particularly important to do projections based on future scenarios of economic activities, with quantitative analysis of transboundary pollution in East Asia.

Cooperation with the United Nations Economic Commission for Europe (UNECE) and the United States Environment Protection Agency should be promoted in order to deal with the intercontinental transport of pollutants in the northern hemisphere, as well as to take measures to deal with the pollutants.

Human health impacts

An hourly value (less than 0.06 ppm) was established as the only environmental quality standard relating to photochemical oxidants in Japan, based on consideration of acute health impacts. As an hourly value, this may be the most stringent standard in the world. Countries that have performed risk assessments based on epidemiological surveys, however, have established eight-hour values as environmental standards, in addition to the hourly values. The government of Japan may need to reexamine its own environmental standards based on such information. For that purpose, it is necessary to conduct epidemiological research on the relationships between photochemical oxidant concentrations and increases in asthma attacks, the number of persons tested for respiratory ailments, and hospitalization. Also important are studies of compound effects of photochemical oxidants and suspended particulate matter, and literature reviews of documents that formed the basis for current environmental quality standards in Europe and North America.

Effects on vegetation

Critical ozone levels must be determined for various types of vegetation in East Asia with a special attention to the sensitivity of representative plant species in the region.

In the face of the large variability in climatic conditions across East Asia, studies must be conducted in various representative ecosystems in the region for observation and modeling of ozone fluxes affecting vegetation. Such studies should reveal the extent of the ozone deposition on vegetation in this region, in interaction with temperature, wind velocity, humidity and CO_2 concentrations. These findings should be incorporated into dynamic vegetation models, which, in combination with atmospheric chemistry and transport models, will facilitate assessments of the present status of ozone impacts on vegetation and projections of future impacts.

This scientific information should underpin policy-making efforts to set up environmental quality standards relating to ozone across East Asia, in order to prevent the worst projections of damage to vegetation from becoming reality.

■Future steps

Measures for reducing NOx and VOC emissions have been promoted and achieved some degree of success in Japan. Despite this success, concentrations of photochemical oxidants have been increasing since around 1980. As shown by the various scientific results described in this booklet, the problem of tropospheric ozone needs to be tackled collectively in East Asia and the entire northern hemisphere.

At present, the Acid Deposition Monitoring Network in East Asia (see next page), with thirteen participating countries, is working with a view to promoting international cooperation to protect the atmosphere in East Asia. As soon as possible, the Network needs to begin careful monitoring of ozone, which as an oxidizing agent is closely associated with acid deposition. In addition to monitoring, a framework including emission inventories and modeling is also needed in order to facilitate integrated assessments. Policy targets also need to be established in order to ensure the protection of the atmospheric environment in the entire region.

Acid Deposition Monitoring Network in East Asia (EANET)

The Acid Deposition Monitoring Network in East Asia (EANET), established in 1998, is an international network for which the main aims are to create a common understanding of the state of the acid deposition problems in East Asia, and to provide useful inputs for decision-making that can prevent or reduce adverse impacts on the environment caused by acid deposition. The Network's Secretariat was established within the United Nations Environment Programme (UNEP). The Acid Deposition and Oxidant Research Center (ADORC), designated as the Network Center for EANET, provides technical support for participating countries.

After a preparatory phase that ended in 2000, EANET started its regular phase activities in 2001. There are thirteen participating countries at present: Cambodia, China, Indonesia, Japan, Lao PDR, Malaysia, Mongolia, Myanmar, Philippines, Republic of Korea, Russia, Thailand and Vietnam. In addition to the implementation of the monitoring of acid deposition and its effects on ecosystems, the Network Center compiles monitoring data and releases it to participating countries and beyond. The first periodic report on the state of acid deposition in East Asia will be completed in 2006. To support participating countries, the Network Center has also conducted joint research projects as well as activities to enhance the reliability of monitoring data.

In addition, to promote regional air quality management, including acid deposition, in East Asia and to provide a sound basis for financial contributions and extending the activities of EANET, discussions are now in progress towards establishment of a regional instrument and further development of the network.

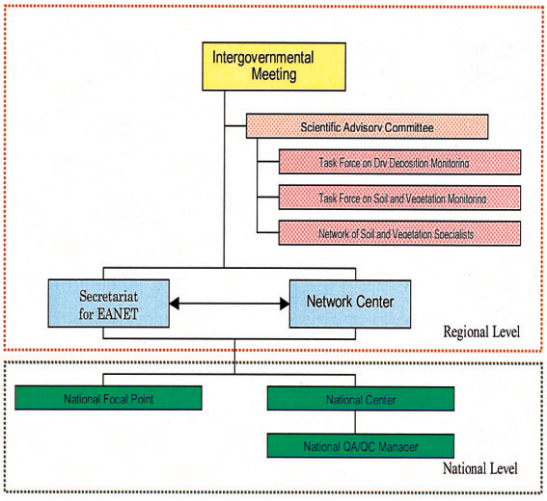


Figure 9-1. Organizational chart of EANET.

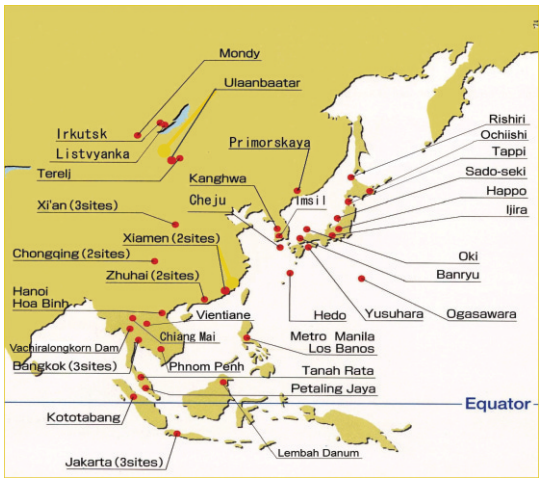


Figure 9-2. EANET monitoring sites (47 sites monitoring wet acid deposition).

Air Quality Standards and other Indexes on Ozone

		Japan Environmental Standard	EHC 7（1978） Guideline	WHO（1998） Guideline	EU-EEA（1998） Criteria	UNECE（2004） Critical level	New Zealand（2002） Guideline
Human Health		0.06ppm （1-hour value）	100～200μg/m³ （0.05～0.1 ppm） （1-hour value）	120μg/m³ （0.06ppm） （8-hour value）	110μg/m³ （0.055ppm） （8-hour value）	120μg/m³ （0.06ppm） （8-hour value）	150μg/m³ （0.075ppm） （1-hour value）
		Warning: 0.12ppm （1-hour value）			Information:180μg/m³（0.09ppm） （1-hour value）	AOT60=0 （1 year）	100μg/m³ （0.050ppm） （8-hour value）
		Serious Warning: 0.24ppm （1-hour value）			Warning:360μg/m³ （0.18ppm） （1-hour value）		
		Emergency: 0.40ppm （1-hour value）					
Plants					200μg/m³（0.10ppm） （1-hour value）		
					65μg/m³（0.033ppm） （24-hour value）		
Agriculture (visible damage)							
	Saturation deficit is less than 1.5kPa					AOT40=0.2ppm・h （5 days）	428μg/m³-h （0.214ppm・h） （5 days）
	Saturation deficit is more than 1.5kPa					AOT40=0.5ppm・h （5 days）	1,070μg/m³-h （0.535ppm・h） （5 days）
Agriculture (yield)				AOT40=3ppm・h (May - July) （5% decrease of yield）		AOT40=3ppm・h （3 months） （5% decrease of yield）	6,420μg/m³-h （3.21ppm・h） （3 months）
Natural/Semi-natural Vegetation				AOT40=3ppm・h (May - July)		AOT40=3ppm・h (May - July) (10% decrease of growth)	6,420μg/m³-h （3.21ppm・h） （3 months）
Forest/Trees				AOT40=10ppm・h （April - September）		AOT40=10ppm・h （April - September） (10% decrease of growth)	21,400μg/m³-h （10.7ppm・h） （6 months）
	In case saturation deficit is small					AOT40=5ppm・h	
	Flux base					1.6n mol/m²/s （1 growth period）	
Sensitive species	Saturation deficit is less than 1.5kPa			AOT40=0.2ppm・h			
	Saturation deficit is more than 1.5kPa			AOT40=0.5ppm・h			
Ecological Risk Assessment				AOT40 Value proper to each receptor			

The standards or indicators that have no category like plants and forest are in the row of human health.

Japan: Notification 25 of the Environment Agency（8 May 1973）. Japan's standard is for photochemical oxidants. Other countries/organizations commonly base theirs on ozone. Serious Warnings in Japan are provided by prefectural governments, based on their own guidelines.

EHC 7(1978): Photochemical oxidants. In: Environmental Health Criteria 7 (1978). International Programme on Chemical Safety (IPCS).

AOT40: Accumulated exposure over a threshold ozone concentration of 40 ppb, when solar radiation 50Wm^2 or more.

SUM60: AOT40 is calculated excluding parts less than 40ppb. SUM60 is calculated including the whole values during the periods more than 60 ppb. The period for the calculation is 12 hours from 8 a.m. through 8 p.m. For assessing acute effects, the total values for three days are used. For long lasting chronic effects, the total values for three months are used. SUM0 is equivalent to the total of all the hourly values.

EU-EEA(1998): Tropospheric ozone in EU - The consolidated report, Topic report No. 8/1998, European Environment Agency.

UNECE: UNECE(2004): Section IX, 1999 Protocol to abate acidification, eutrophication and ground-level ozone. In: Handbook for the 1979 convention on long-range transboundary air pollution and its protocols.
Karlsson et al. (2003): Establishing ozone critical levels II - UNECE Workshop Report. IVL Report B 1523.
Fuhrer et al.(1997): Critical levels for ozone effects on vegetation in Europe. Environ. Pollut. 97(1-2): 91-106.

New Zealand (2002): Ambient air quality guidelines, 2002 Update, Air quality report No.32, Ministry of the Environment. May, 2002.

	USA（1979） Standard	USA（1997） New standard	California（2004） Standard	Canada Guideline	UK Standard	China (1996) Standard	R. of Korea Standard	Thailand Standard
	0.12ppm （1-hour value）	0.08ppm （8-hour value）	0.09ppm （1-hour value）	Maximum Desirable: 51ppb （1-hour value）	100μg/㎥ （0.05ppm） （8-hour value）	Class I Standard 0.12mg/㎥ （0.06ppm） （1-hour value）	0.06ppm （8-hour value）	0.10ppm （1-hour value）
			0.070ppm （8-hour value）	Maximum Desirable: 15ppb （24-hour value）		Class II Standard 0.16mg/㎥ （0.08ppm） （1-hour value）	0.1ppm （1-hour value）	0.04ppm （yearly value）
				Maximum Acceptable: 82ppb （1-hour value）		Class III Standard 0.20mg/㎥ （0.10ppm） （1-hour value）		
				Maximum Acceptable: 25ppb （24-hour value）				
				Maximum Acceptable: 15ppb （Yearly Average）				
				Maximum Tolerable Level: 153 ppb （1-hour value）				
	0.12ppm （1-hour value）	0.08ppm （8-hour value）				Class I Standard 0.12mg/㎥ （0.06ppm） （1-hour value）		
						Class II Standard 0.16mg/㎥ （0.08ppm） （1-hour value）		
						Class III Standard 0.20mg/㎥ （0.10ppm） （1-hour value）		
				SUM60=0.5-0.7ppm･h (12 hours,3 months）				
				SUM60=5.9-7.4ppm･h (12 hours,3 months）				
				SUM60=4.4-6.6ppm･h (12 hours,3 months）				

USA: Although the primary and secondary air quality standards have the same value, the primary standard targets human health and the secondary standard targets visibility, plants, animals, and buildings. In this table, the latter is in the row of plants, because agricultural products are not clearly distinguished in the standard. The standards revised in 1997 are applied for the three-year average of the fourth largest value in a year of maximum daily 8-hour average values, which should be less than 0.08 ppm. However, for sites where consecutive three-year data do not attain the hourly value, the previous hourly value is applied.

California, USA (2004) : Recommendation for an ambient air quality standard for ozone. Office of Environmental Health Hazard Assessment, California Environmental Protection Agency. June 2004.

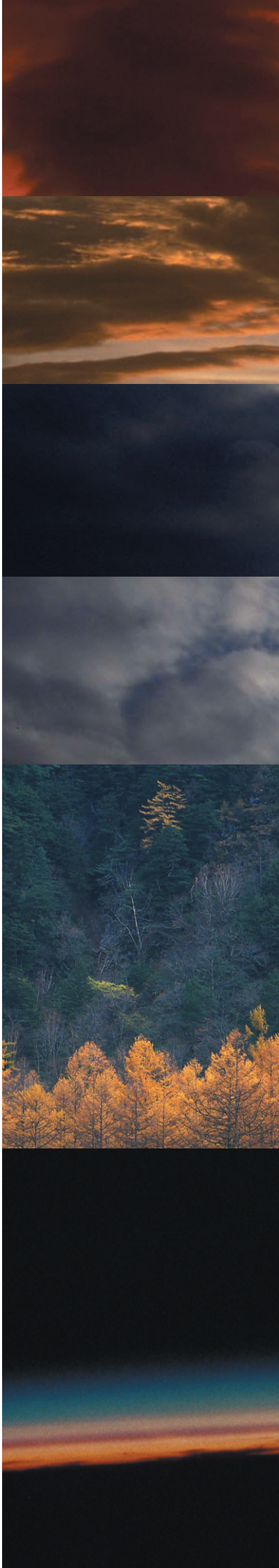
Canada: LOAEL (Lowest Observable Adverse Effect Level) values are used as the recommended values for plants. National ambient air quality objectives for ground-level ozone - Summary Science Assessment Document, Environment Canada (1999).

UK: Daily maximum of 8-hour average should not exceed the standard 10 times a year. At the present, ozone is not targeted in regulation.

China: Ambient air quality standard. GB 3095-1996. Class I standard targets natural reserves, places of scenic beauty and special protection areas. Class II standard targets residential areas, commercial and traffic areas, cultural areas, industrial areas and rural areas. Class III standard targets specified industrial areas.

Ecological risk assessment: Five-year average AOT40 value during a period specific to each targeted item.

Critical level for flux base: This was discussed at UNECE workshop in 2002 and adopted as provisional Critical Level I.



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