

Chapter 4

MONITORING AND SIMULATION

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4.1 CONTINUOUS MONITORING

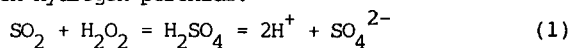
As mentioned in earlier chapters, there are air quality standards for five air pollutants in Japan, that is, sulfur dioxide (SO_2), carbon monoxide (CO), suspended particulate matter (SPM), photochemical oxidants (O_x), and nitrogen dioxide (NO_2). The measurement methods for these pollutants discussed in this chapter are employed at more than 1,000 monitoring stations in Japan.

In addition to these pollutants, measurement methods for nitric oxide (NO) and non-methane hydrocarbons (NMHC), which are measured at several hundred monitoring stations, will be mentioned briefly.

4.1.1 Sulfur dioxide

Sulfur dioxide is produced by the oxidation of sulfur in fossil fuels during combustion. The conductometric method is taken as the reference method for SO_2 measurement in Japan. As substances which are electrolytes in aqueous solution affect the conductivity of the solution, the observed change in the conductivity of the solution will be the sum of the effects of all the ions in the solution. If the concentrations of all other electrolyzing gases are assumed to be either constant or relatively insignificant, the change in the conductivity can be related to the SO_2 concentration.

After passing through a dust filter and a flow meter, an air sample is introduced into an absorbing solution of hydrogen peroxide. Sulfur dioxide gas reacts with hydrogen peroxide:



The increased conductivity produced by the additional hydrogen and sulfate ions is related to the sulfur dioxide concentration. The hydrogen peroxide solution is acidified with 1×10^{-5} N sulfuric acid to reduce the interference from CO_2 . Air pollutants such as Cl_2 , HCl, NO_2 , H_2S , and HF produce positive errors in SO_2 measurements, while NH_3 produces negative errors. High concentrations of ammonia gas are often found in industrial areas and farming regions. In such areas, an ammonia scrubber made of ion-exchange membrane or oxalic acid pellets

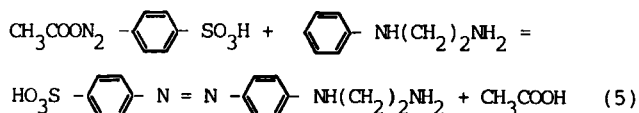
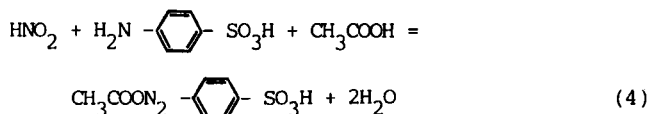
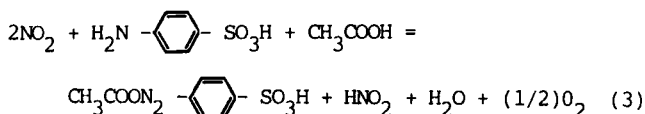
is added prior to the SO_2 absorption to eliminate the NH_3 interference.

The pararosaniline wet chemical method is employed as a reference method in the USA. Sulfur dioxide in the air sample is absorbed in a potassium tetrachloromercurate solution and converted to a monochlorosulfonatomercurate complex. Pararosaniline and formaldehyde react with the complex to form pararosaniline methyl sulphonic acid which is an intensely colored dye. The absorption of the dye is measured spectrophotometrically at 560nm.

4.1.2 Nitrogen oxides

Six types of oxidized nitrogen are chemically stable, including N_2O , NO , N_2O_3 , NO_2 , N_2O_5 and NO_3 . Nitrogen dioxide (NO_2) and nitric oxide (NO), which are primarily generated by combustion, are considered to be air pollutants. Nitrogen oxides (NO_x) by convention are indicated as the sum of NO and NO_2 concentrations. Nitrogen oxides in ambient air can be measured either by wet chemical or by chemiluminescent methods.

The use of Saltzman reagent, which is one of the wet chemical methods, is the reference method for measurements of NO_2 and NO in Japan. Nitrogen dioxide in the air sample is absorbed in the Griess-Saltzman azo-dye-forming reagent (a mixture of sulfanilic acid, N-(1-naphthyl)-ethylenediamine dihydrochloride and acetic acid) which develops a red-purple color. The amount of reduced NO_2 in the solution is determined spectrophotometrically by measurement at 550nm. Nitrogen dioxide reacts with the azo-dye-forming reagent as follows:



If reactions (2), (4), and (5) occur, 2 moles of NO_2 produce 1 mole of azo-dye and if reactions (3), (4), and (5) occur, 2 moles of NO_2 are converted to 2 moles of azo-dye. The conversion ratio of NO_2 molecules to azo-dye molecules is 0.5 in the first case and 1.0 in the second case. As both reactions occur simultaneously in actual measurement, the ratio is usually empirically determined in practice. The ratio was reported as 0.72 in

Saltzman's original paper, but the value of 0.84 is currently used in Japan.

NO does not react with the azo-dye-forming reagent, but can be measured by oxidising to NO₂ by passing through acidic potassium permanganate solution. In the continuous Saltzman monitor, nitrogen dioxide in the air sample is absorbed by the azo-dye-forming reagent after passing through a filter and a flow meter. The absorption of the developed color produced by the reaction between NO₂ and the reagent is measured to determine the NO₂ concentration in the air sample. The remaining air containing NO is introduced into an oxidation chamber. Finally it is bubbled through more azo-dye-forming reagent where the oxidized NO reacts to form the azo-dye complex. Average concentrations of NO₂ and NO are measured by replacing the azo-dye-forming reagent contained at hourly intervals. Sampling of NO and NO₂ and development of color are done simultaneously in the Saltzman method.

In the Jacobs-Hachheiser method or its modification, NO₂ in the air sample is collected in a sodium hydroxide solution for 24 hours and subsequently analyzed in the laboratory by adding a mixture of phosphoric acid, sulfanilamide and N-(1-naphthyl)-ethylenediamine dihydrochloride. The absorption of the resultant colored solution is measured at 540nm.

In addition to these wet chemical procedures for NO₂ analysis, a gas phase chemiluminescent method has been used widely in recent years. Fundamentally, the wet chemical procedure analyzes NO₂, while the chemiluminescent method measures NO concentration as follows:



NO in filtered air sample is drawn into the reaction vessel and rapidly mixed with O₃. Chemiluminescent reactions (6) and (7) take place in the vessel and the intensity of the emitted light is measured by a photo-multiplier tube. For NO₂ analysis, the air sample containing NO and NO₂ is introduced into a converter to reduce NO₂ to NO. The reduced gas is then directed into the reaction vessel. Thus NO_x concentration is measured and NO₂ concentration can be calculated by subtracting the concentration of NO from that for NO_x.

4.1.3 Carbon monoxide

Carbon monoxide is produced by incomplete combustion. The carbon monoxide concentration in ambient air can be measured by non-dispersive infrared absorption or by a gas chromatographic method.

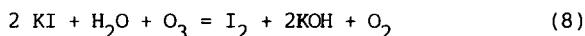
The non-dispersive infrared absorption method is the Japanese reference method. Molecules of different elements such as CO absorb infrared radiation at specific wavelengths, so non-dispersive infrared spectroscopy can be used for measuring CO. Infrared radiation is passed through two cells, a sample cell and a reference cell. Pure nitrogen gas is contained in the reference

cell, while CO in the air sample is pumped through the sample cell. The CO in the air sample absorbs some of the infrared radiation at a specific wavelength while the remaining infrared energy passes through to a dual cell detector located behind the sample and reference cells. The dual cell detector is filled with pure CO so that it is sensitive only to the infrared radiation at the absorbing wavelength. The detector cells are separated by a thin metallic film. The infrared beams passing through the sample cell and the reference cell are separately absorbed by each cell of the detector. The detector on the sample cell side receives less energy than that on the reference cell side due to the removal of energy by CO in the air sample. The thin metallic film is displaced to compensate for the difference in pressure of pure CO gas on both sides caused by the imbalance of the intensity of the impinging infrared beams. The displacement causes the change in capacitance which generates an electrical signal.

The gas chromatographic method with a flame ionization detector (FID) can also be used to measure CO in ambient air. Volatile organic compounds are measured by the FID by introducing samples into a hydrogen flame burning in air. Proportional changes in an induced electric field across the flame are measured as the volatile compounds burn in the flame. Carbon monoxide, which is not detected by the FID, is first reduced to methane in a catalytic column and then detected by the FID after it has been separated from other compounds in the sample by a separation column.

4.1.4 Photochemical oxidising agent (Ozone)

The neutral, buffered, potassium iodide method (NBKI) is used as the reference method for oxidising agents in Japan. The absorption of oxidising substances, mainly ozone, in the neutral buffered potassium iodide solution yields iodine by the following reaction:



The absorption of iodine at 365 nm indicates the concentration of the oxidising agents in the air sample.

In a continuous oxidising agent monitor. The filtered sample reaches the absorption vessel through a CrO_3 oxidizer where sulfur dioxide in the air sample is oxidised to sulfuric acid. Sulfur dioxide interferes with the oxidising agent measurements by reducing the iodine produced by reaction (8). In the absorption vessel, the air sample and potassium iodide solution flow in a counter-current direction. The absorption of the potassium iodide solution before and after contact with the air sample are compared and the difference indicates the concentration of oxidising agents in the air sample.

The solution is repeatedly used after removing iodine by means of an activated charcoal filter. Nitrogen dioxide and nitric oxide which are

oxidised by the CrO_3 oxidiser produce a positive error in the oxidising agents measurements.

The chemiluminescent analytical procedure is based on the chemiluminescent reaction of ozone with ethylene. Ethylene and ambient air containing ozone are introduced into a mixing vessel where the ozone reacts quantitatively with the ethylene to emit light, which is detected by a photomultiplier tube.

4.1.5 Suspended particulate matter

Suspended particulate matter is defined as suspended particles of diameter less than $10\text{ }\mu\text{m}$. Particles smaller than $10\text{ }\mu\text{m}$ are respirable and remain suspended in the atmosphere for a significant period of time. The reference method for measuring the suspended particulate matter specifies the use of a low volume sampler to draw air at a flow rate of 20 l/min through a glass fiber filter for 24 - 48 hours. The mass concentration of the suspended particulate matter is calculated in $\mu\text{g/m}_3$ from the mass of collected particles and the volume of air sampled. A cyclone or a cascade impactor is used to exclude particles larger than $10\text{ }\mu\text{m}$ from the air stream prior to the fiber filter.

Errors in this method mainly come from 1) weighting errors, 2) non-uniform air flow and 3) non-uniformity of the separation of fine and coarse particles. A difference in the water content in the filter before and after the sampling is one of the basic errors encountered in weighing. The filters should be allowed to reach equilibrium at the same temperature and humidity prior to each weighing. If the filters are stored for a long time after sampling, mass may be lost due to evaporation of volatile substances. Static charges sometimes cause positive or negative errors in the mass measurement of lightly loaded filters. Therefore, any static charge on the filter should be neutralized with a Po^{210} source. A sharp decrease in air flow may occur during sampling if the particulate matter is oily or wet. The air flow rate should be checked frequently or controlled electronically. Non-uniformity of the separation of fine and coarse particles results in large deviations of the mass concentration in the presence of coarse particulates, since the mass of a particle of unit density is proportional to the cube of its diameter.

Suspended particulate matter can be measured by methods other than gravimetric measurement. The attenuation of beta radiation can be applied to the mass concentration measurement. Direct reading instruments for real time measurement include the light scattering method and the piezo-balance method. These methods are also the reference methods in Japan within the range where they show linear relation with the gravimetric method. The scattered light intensity of a single particle is a function of its particle diameter (d), refractive index and the wavelength (λ) of the light used. For particles

which are small in diameter d compared with the wavelength λ , the scattering intensity is directly proportional to d^6 and inversely proportional to λ^4 . With increasing particle diameter, its dependence on the particle diameter becomes less. If the characteristics of the sample particles, such as diameter distribution, refractive index and absorption efficiency of light, are reproducible, the light scattering method may be employed for ambient air monitoring after calibration against the gravimetric method. In the piezo-balance method, particles are pumped to a quartz crystal surface and deposited on it by electrostatic precipitation. The mass change of the crystal in an oscillator circuit changes its resonant frequency; the rate of frequency change reflects particulate mass concentration in the air sample. In applying this method to ambient air monitoring, loss of sensitivity due to high particle loading on the crystal surface and interference of absorbed water vapor should be taken into account.

4.1.6 Non-methane hydrocarbons

Various kinds of hydrocarbons are found in the atmosphere. Some of these are carcinogens and/or take part in photochemical oxidation.

Methane is a natural atmospheric gas exceeding 1 ppm which is released by the activity of methane producing bacteria, so only non-methane hydrocarbons are considered to be air pollutants. Many techniques using gas chromatography with a flame ionization detector (FID) have been developed for total non-methane hydrocarbon analysis and for specific hydrocarbon components.

Two types of GC/FID configurations have been used in Japan for automated analysis of ambient non-methane hydrocarbons; one is a differential method and the other is a direct method. In the differential method, the concentration of non-methane hydrocarbons is determined by subtracting the methane concentration from the concentration of total hydrocarbons (THC). The air sample is first introduced directly into the detector for the THC analysis, then sample of methane provided from a separation column is fed to the detector by a switching valve. Oxygen can interfere with the differential method. Oxygen and hydrocarbons in the air sample are introduced into the FID at the same time. These react to produce CO and CO₂ to which the FID is insensitive.

In the direct method non-methane hydrocarbons are separated from oxygen prior to entering the detector. As the separation column separates many components of the air sample according to their molecular weights in general (for example, inorganic compounds, methane and heavier organic components) many peaks of non-methane hydrocarbons are detected if the separation column feeds directly into the detector. If the carrier gas flow direction is reversed after the elution of methane, a plug of non-methane hydrocarbons is obtained at the opposite end of the separation column. By reversing the direction of the

carrier gas flow and by switching the connections to the separation column and the detector, methane and non-methane hydrocarbons are analyzed directly. The oxygen interference is thus avoided.

4.2 PASSIVE MONITORING

Spatial and temporal variations of air pollutant concentrations may be so great that monitoring stations must be carefully sited in order to provide data representative of their region. How are the representative locations determined? How many monitoring stations are required to obtain full knowledge of the air quality? The potential number of continuous monitors in operation is limited by the costs of installation and maintenance although the continuous monitoring methods described in the previous section are well developed. Simple and inexpensive monitoring devices have been developed for simultaneous measurements of air pollutant concentrations at many locations over long periods of time. Even if these simple devices are less accurate than the continuous monitors, they are very useful for providing an overview of the air quality in an area of interest.

A passive monitor which can measure air pollutant concentrations without a pump can provide simultaneous pollution measurements at many locations. The application of the passive monitor is not limited to outdoor measurements. People spend most of their time indoors, so the importance of indoor air quality has become a significant public health issue in recent years. As indoor air quality is primarily determined by the emission rate from indoor pollutant sources, the air exchange and removal rates, and by outdoor pollutant concentrations, air quality can vary widely from house to house. It is therefore necessary to collect large amounts of data in order to obtain statistically reliable exposure estimates. The passive monitor is particularly well suited for large scale indoor and personal exposure measurements as well as for outdoor measurements because it is structurally simple, silent and inexpensive.

The main difference between passive and active (continuous) monitors is the means by which pollutants are transferred from the atmosphere to the collecting material. In the active monitor, pollutants in the air sample are drawn into the collecting material by a pump, while pollutants are transferred by molecular diffusion in the passive monitor. Pollutants collected by the passive monitor are often analyzed by the same chemical procedure as the active monitor, so the diffusion process is an essential part of the passive monitor. If the diffusion rate or the sampling rate of the passive monitor is well characterized, the pollutant concentrations can be quantitatively measured by the passive monitor. I will describe the theoretical background of the diffusion process to obtain quantitative results and then introduce several

widely used devices.

4.2.1 Theoretical analysis of the passive monitor

(i) Analogy of the diffusion process with electric resistance. The diffusion process is described by Fick's law. The concentration, C (mole/cm³), of the air pollutant of interest with respect to the one-dimensional position, x (cm), and time, t (s) becomes:

$$\frac{dc}{dt} = \frac{d}{dx} \left(D \frac{dc}{dx} \right) \quad (9)$$

where D is the diffusion coefficient.

The eddy diffusion coefficient in turbulent gas flow ranges from 100 to 10000 (cm²/s), while the molecular diffusion coefficient is of the order of 0.1 (cm²/s). Therefore, it is a reasonable assumption that a concentration gradient exists only in the region of molecular diffusion around the sorbent of the passive sampler. Under a steady state condition, integration of equation (9) with boundary conditions of $X = 0$, $C = C_o$, and $X = L$, $C = C_a$ gives:

$$N = (D/L) (C_a - C_o) \quad (10)$$

where C_o is the concentration at the surface of the sorbent, L indicates the thickness of the region of molecular diffusion and C_a is the concentration outside the region. N is the mass flow rate per unit area, which is often called the mass flux. If N is thought of as a current, equation (10) is similar to Ohm's law. The difference in concentration ($C_a - C_o$), which is the driving force of the flow, is comparable to the voltage difference.

Mass Flux	Current	
Concentration	Voltage	(11)

The proportional coefficient of current and voltage is resistance. In our case, resistance is expressed as follows:

$$R = L/D \quad (12)$$

The unit of R for mass transfer is (s/cm). The reciprocal of R , then, has the same units as velocity. When we expose an absorbent of area A (cm²) to the air for a period t (s), the amount of absorbed air pollutant M (mole) becomes:

$$M = N * A * t = (A/R) * (C_a - C_o) * t \quad (13)$$

The units of A/R are (cm³/s) which are the same as for the flow rate of the active sampler. The area, A , and the sampling period, t , are the operational variables, so characteristics of the diffusion process involve the resistance R shown in equation (13).

(ii) Model of the passive sampler. There are usually three regions around the sorbent of the passive monitor where air pollutants can diffuse by molecular diffusion (Fig. 4.1). This implies that there are three types of resistance in the process of air pollutants diffusing from the air to the sorbent. Air pollutants collected by the sorbent must pass 1) a boundary layer

around the interface of the air and the passive monitor (R_1), 2) a stagnant region produced by a diffusion barrier (R_2) and 3) a boundary layer at the sorbent (R_3).

These resistances connect in series. By analogy with electrical resistance, the overall resistance (R_o) of the diffusion becomes:

$$R_o = R_1 + R_2 + R_3 \quad (14)$$

The reciprocal of R_o is often called an overall mass transfer coefficient ($K_{og} = 1/R_o$). If a very small amount of the air pollutant of interest is absorbed, it is a reasonable assumption that C_o in equation (13) is nearly equal to zero, equation (13) then becomes:

$$M = (A/R_o) * C_a * t = K_{og} * A * C_a * t \quad (15)$$

which allows us to easily calculate the pollutant concentration during the sample exposure period (t).

(iii) Descriptions of diffusion resistance by physical parameters. Unless a chemical reaction occurs at the boundary layer in the gas phase region, R_1 could be described by the following equation:

$$R_1 = b/D \quad (16)$$

Here, b is the thickness of the boundary layer and g stands for gas phase. In the same manner R_2 becomes:

$$R_2 = L/(D * v) \quad (17)$$

where L and v are the length of the diffusion barrier and the void fraction of the barrier, respectively.

If the reaction between the air pollutant of interest and the absorbent is first order, irreversible and rapid, with reaction rate of k (1/s), then the

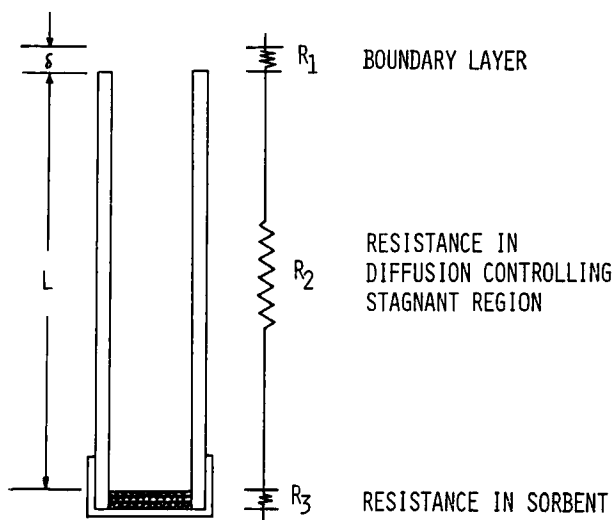


Fig. 4.1. A model of passive sampler.

third resistance becomes:

$$R_3 = m/(k \cdot D_L)^{1/2} \quad (18)$$

where m is Henry's constant and D_L is the diffusion coefficient in the liquid phase.

(iv) Effects of environmental factors on physical parameters. Surface wind velocity, temperature and relative humidity are the three major environmental factors affecting the physical parameters.

Surface wind velocity (WV) has an effect on the thickness of the boundary layer b . If the air stream is laminar and incompressible, the thickness of the boundary layer near the leading edge of a flat plate can be described by the distance from the leading edge and the kinetic viscosity. In most cases, air flow indoors and outdoors is not laminar; therefore, we cannot predict the thickness of the boundary layer. It should be examined experimentally.

The diffusion coefficients and the chemical reaction rate constant are functions of temperature. Kinetic theory shows that the diffusion coefficient in an ideal gas is proportional to $T^{3/2}$ where T indicates absolute temperature. In a real gas mixture, the exponent of T is slightly larger than $3/2$. The theory to predict the gas phase diffusion coefficient at a specific temperature is well developed. For example, if the Lenard-Jones potential parameters for the binary gas mixture are known, the diffusion coefficient is calculated from the equation derived by Hirschfelder et al.² On the other hand, development of the theory to estimate the diffusion coefficient in the liquid phase is insufficient. The reaction rate constant increases exponentially with elevation of temperature following Arrhenius' law.

If the relative humidity affects the water content of the sorbent, then the diffusion coefficient in the liquid phase and the reaction rate constant may be changed. The exact relation between them is not clear yet.

Overall resistance to the diffusion process in the passive monitor could be described as functions of these environmental factors:

$$R_o(WV, T, RH) = b(WV)/D(T) + L/D(T) + m(T)/(k(T, RH) \cdot D_L(T, RH))^{1/2} \quad (19)$$

Only the length of the diffusion barrier, L , can easily be controlled (eqn. 19). For very large values of L , we can suppress the variation of the first and third terms due to change in the environmental conditions. However, if the second term is very large, the sensitivity of measurements which are proportional to the reciprocal of R_o , that is, K_{of} , is lowered. Therefore, we have to determine an appropriate length for the diffusion barrier. Of these environmental factors, the influence of the surface wind velocity on the overall resistance has been well examined empirically.

4.2.2 Lead peroxide candle method

The lead peroxide candle method³ developed in 1934 is a semi-quantitative method for ambient sulfur dioxide measurement. In this method, the ambient sulfur dioxide concentration is not expressed in parts per billion but as the sulfation rate [$\text{mg SO}_3/(\text{day} \times 100\text{cm}^2 \text{ PbO}_2)$]. Nevertheless, this method provides a useful historical overview of sulfur oxide pollution. For example, Fig. 4.2 shows sulfur oxides concentrations in some urban and industrial areas in Japan since 1957. Although the monitoring method is semi-quantitative, the results indicated well the progress of industrialization and the worsening of air quality.

The underlying principle of the method is to measure the amount of sulfate produced by the reaction :



An activated paste containing lead peroxide is homogenized in gum tragacanth. This is coated on cotton gauze which is then wrapped around a porcelain cylinder to form a candle. The candle held in a shelter is exposed to polluted air for one month to absorb SO_2 . After exposure, the cotton gauze is soaked in sodium carbonate solution to dissolve the lead sulfate. The lead sulfate filtered from the lead peroxide solution is acidified with hydrochloric acid. After removing the carbonate ions, barium chloride solution is added and then

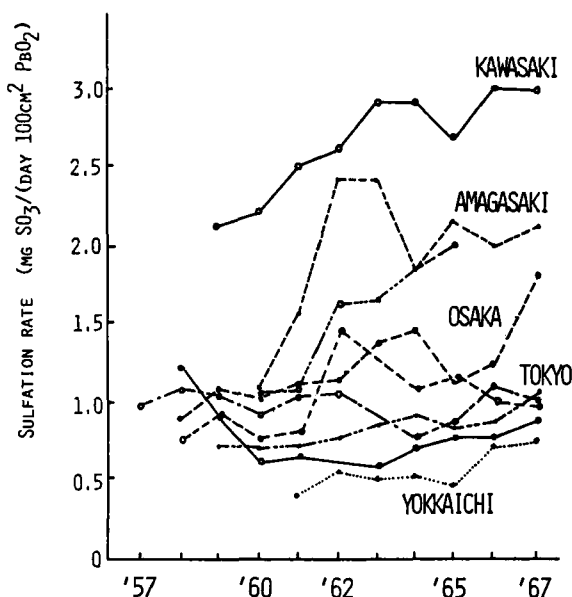


Fig. 4.2. Sulfur oxide concentration in '60s measured by lead peroxide candle method.

the resulting barium sulfate is weighed.

The sulfation rate is calculated as:

$$\begin{aligned} \text{Sulfation rate [mgSO}_3\text{/(day} \times 100 \text{ cm}^2 \text{ PbO}_2\text{)]} \\ &= (W_1 - W_2) \frac{3}{80} \frac{233}{233} \times (100/a) \times (1/n) \\ &= 34.3 \times (W_1 - W_2)/(a \times n) \end{aligned} \quad (21)$$

where W_1 and W_2 are the weights of BaSO_4 in the sample and the blank, respectively. 'a' is the area of PbO_2 exposed to the air and n is the exposure period.

Further studies are required for monitoring the sulfur oxide concentration quantitatively by this simple, inexpensive method.

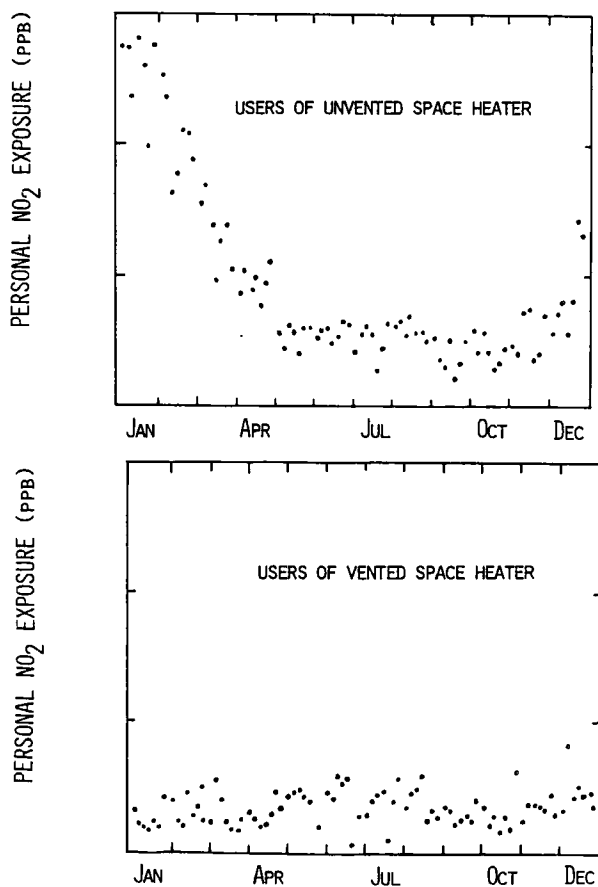


Fig. 4.3. Seasonal change of personal NO₂ exposures of users of unvented or vented space heaters.

4.2.3 Filter badge and palmes tube

The filter badge⁵ and the Palmes tube⁶ were developed for quantitative measurements of outdoor and indoor NO_2 concentrations and personal exposures to NO_2 . For example, Fig. 4.3 shows the seasonal change in daily averages of personal NO_2 exposures measured by the filter badge.⁷ A housewife and her neighbor living in a residential area in Tokyo were exposed to considerably different levels of NO_2 though outdoor NO_2 concentrations around their houses were the same. They used different types of space heaters. The Palmes tube is simpler in configuration, but less sensitive than the filter badge. I will explain the details of the filter badge here; the Palmes tube is described elsewhere.

The filter badge consists of three parts: a badge case, an absorbent sheet and a diffusion controlling mat (Fig. 4.4). The badge case has an opening to the air on one side. The absorbent sheet is made from a cellulose fiber filter paper containing a triethanolamine solution to absorb NO_2 gas. The diffusion controlling mat is a filter of hydrophobic fiber made of a fluorine containing polymer. Since the filter has an average pore size of $5\text{ }\mu\text{m}$, the transfer of gas through the mat appears to be by molecular diffusion; thus the diffusion velocity controls the absorption rate.

After exposing the filter badge to the atmosphere, the absorbent sheet is put into a glass-stoppered cylinder and soaked in azo-dye-forming reagent. The azo-dye-forming reagent is a mixture of sulfanilic acid, concentrated phosphoric acid and N-(1-naphtyl)-ethylenediamine dihydrochloride solution. After allowing 40 min for complete color development at $25 - 30^\circ\text{C}$, the absorbance is measured at 545 nm .

The performance of the filter badge was examined by using a wind tunnel. When the absorbent sheet was directly exposed to the standard NO_2 gas in the wind tunnel, the absorption rate at a wind velocity of 4.0 m/sec was 2.7 times as great as the absorption rate at 0.15 m/sec . The absorption rate might be

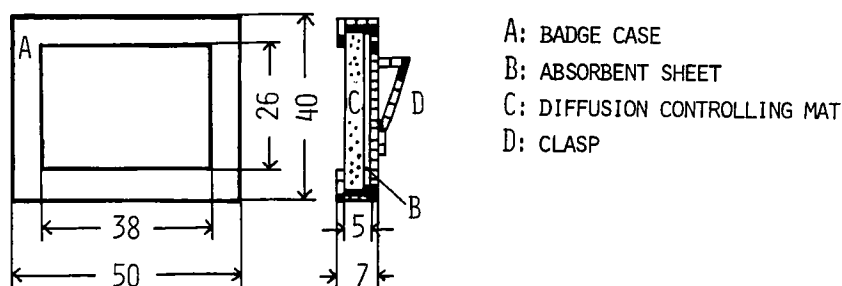


Fig. 4.4. Filter badge for measurement of nitrogen dioxide.

enhanced by turbulent mixing at high wind velocity. The difference in the absorption rates decreased as more layers were applied; however, at the same time the absorption rate itself decreased. The optimum number of layers was determined using the criteria that the effect of wind velocity should be sufficiently suppressed, and that the sensitivity should be adequate.

The effect of the relative humidity on the absorption rate was also examined. The absorption rate varied about 20%, with the relative humidity ranging from 40% to 80%. The overall mass transfer coefficient was highest at a relative humidity of 60%, but its variation due to relative humidity was less than that due to wind velocity.

The filter badge method was compared with the Saltzman continuous monitor by changing the sampling period from one day to seven days. Nitrogen dioxide concentrations measured with the filter badge method were nearly equivalent to the results obtained from the Saltzman method (Fig. 4.5). According to these comparative tests, the filter badge can remain effective after 7 days' exposure. It may be possible to expose for up to one month.

4.3 ATMOSPHERIC MODELS

What is the most cost effective way to maintain acceptable air quality? Air quality control requires a lot of money, labor, and significant technical development. These are very controversial political, economical and technological issues. There are several alternatives for maintaining adequate air quality; for example, a change of energy sources, installation of pollution control equipment in automobiles and industrial plants, relocation of industries, etc. Simulation modeling of the present environmental air quality

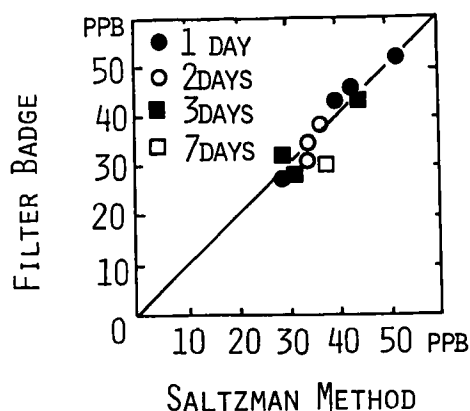


Fig. 4.5. Comparison of filter badge and Saltzman method.

and of future trends is a useful way to determine how to meet air quality standards best.

The behavior of pollutants emitted from specific sources is a complicated function of meteorological and source emission conditions. This behavior can be physically described by a diffusion equation using meteorological conditions as parameters. The meteorological conditions, however, can fluctuate so quickly and widely that we cannot feed raw meteorological data directly into the model, even using a very large computer. One must simplify the meteorological and source conditions into several categories. A theoretical explanation of a dispersion model and the categorization of meteorological and source emission conditions will be briefly described in the following sections.

4.3.1 Dispersion model

The concentration of pollutant released from a stack on a flat surface, is given by equation (22) assuming a steady state (Fig. 4.6).

$$c(x, y, z) = \frac{Q}{2\pi s_y s_z U} \exp\left(-\frac{y^2}{2s_y^2}\right) \times \left(\exp\left(-\frac{(z+H)^2}{2s_z^2}\right) + \exp\left(-\frac{(z-H)^2}{2s_z^2}\right)\right) \quad (22)$$

This equation is commonly used to calculate the concentration, $C(\text{g/m}^3)$, of gaseous or particulate pollutants of small diameter at a point (x, y, z) in a buoyant plume from an effective stack height, H , which is the sum of physical

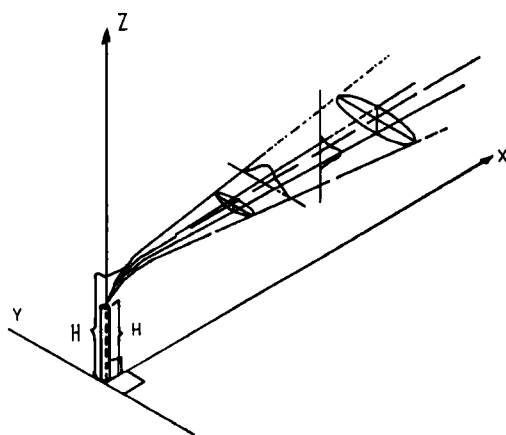


Fig. 4.6. Coordinated system for Gaussian dispersion of plume.

stack height and plume rise. This equation, the so-called Gaussian plume equation, is derived with the following assumptions.

The first assumption is that the spatial profile of the average pollutant distribution has a normal (Gaussian) distribution with a standard deviation of s_y horizontally and s_z vertically. Both are determined by the meteorological conditions. Secondly, the mean wind velocity, U (m/s), is high enough to ignore the diffusion effect in the downwind direction. Thirdly, pollutants, once discharged from a stack, are conserved and are reflected completely rather than being absorbed by the earth's surface. The final assumption is that the pollutant emission rate, Q (g/s), is uniform and continuous for a longer period than the travel time to any specific downwind position.

The actual profile of the plume, which is governed by the vertical distribution of temperature and wind does not always fit the Gaussian distribution as shown in Fig. 4.7,⁹ but the plume model is still useful for calculating an average concentration over a relatively long period.

If the mean wind velocity, U , is zero or very small (U less than 1m/sec), the diffusion effect cannot be ignored in comparison with the advection effect. Dispersed pollutant concentrations emitted from an instantaneous source with low mean wind velocity are estimated using the puff equation.

$$c(x, y, z) = \frac{Q'}{(2\pi)^{3/2} s_x s_y s_z} \exp\left(-\frac{(x-ut)^2}{2s_x^2} - \frac{y^2}{2s_y^2}\right) \times \left(\exp\left(-\frac{(z+H)^2}{2s_z^2}\right) + \exp\left(-\frac{(z-H)^2}{2s_z^2}\right)\right) \quad (23)$$

Here, t (s) is the time elapsed since a puff emission and Q' (g) is the mass emitted from the instantaneous source. The pollutant concentration at the particular point is described by the model as the superposition of many puffs discharged before that time.

The plume and puff equations are basic model equations, so many derivative equations are employed for specific conditions.

4.3.2 Parameters of the dispersion model

The parameters used in eqns. (22) and (23) to determine the pollutant concentration at a particular point (x, y, z) must be related to the stability of the atmosphere and the source emission conditions.

(i) Stability of the atmosphere. If a parcel of dry air moves freely upward in a hydrostatically stable environment and expands slowly without exchanging heat with its environment (i.e. adiabatic expansion), its temperature decreases 0.98 °C per 100 m of elevation. This adiabatic rate of temperature decrease,

the adiabatic lapse rate, is obtained from the hydrostatic equation (eqn. 24) and the first law of thermodynamics (eqn. 25).

$$\frac{dP}{dz} = -\rho g \quad (24)$$

$$0 = C_p dT - \frac{1}{\rho} dP \quad (25)$$

The observed rate of temperature change with height is called the environmental (temperature) rate. If the environmental rate of temperature decrease is the same as the adiabatic lapse rate, then an adiabatically displaced parcel is said to be in neutral equilibrium as it is moved upward.

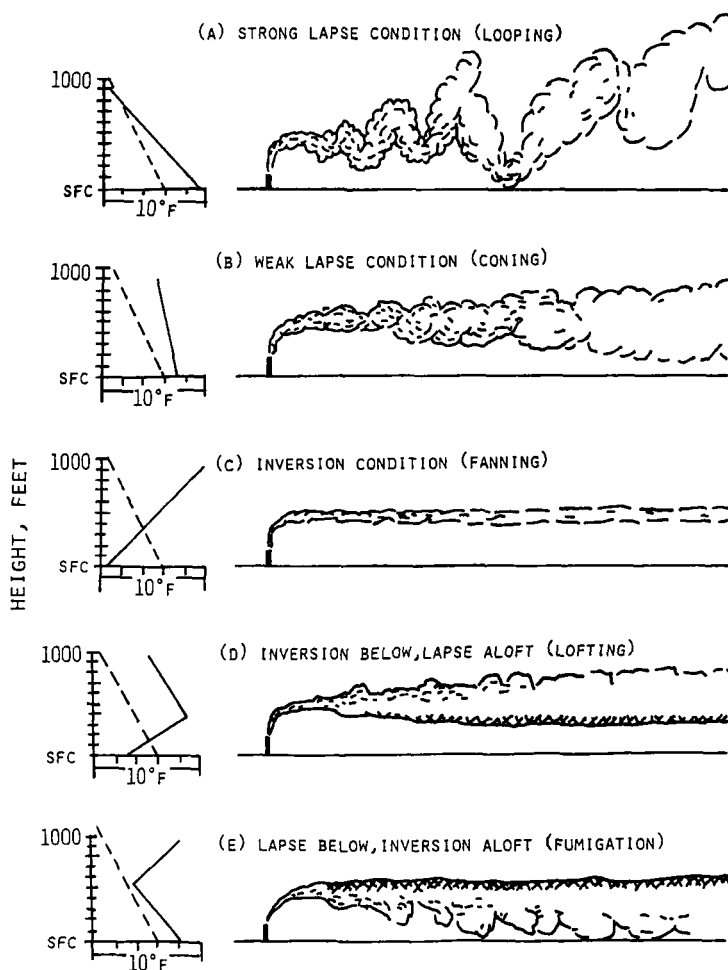


Fig. 4.7. Stack gas behavior under various conditions of stability.

When the environmental temperature rate decreases faster than the adiabatic lapse rate, then an air parcel moving upwards becomes warmer and less dense than the surrounding environment. The parcel is in unstable equilibrium and accelerates upward, powered by buoyancy forces. On the other hand, if the environmental temperature decreases at less than the adiabatic lapse rate (or even at a negative rate), the parcel is in stable equilibrium and is forced back to its starting height by (anti) buoyancy forces.

When an air parcel at temperature T is brought adiabatically from a pressure P to sea-level pressure P_o (100 KPa), the temperature of the parcel becomes its potential temperature which is often used to express the vertical temperature profile. By substituting $(1/O)$ in eqn. (25) with $(1/O) = RT/P$ derived from the equation of state for the atmosphere and by integrating from the sea-level pressure P_o to the pressure at any level, the potential temperature is calculated as follows:

$$T_p = T * (P_o/P)^{R/C_p} \quad (26)$$

The vertical gradient of the potential temperature (dT_p/dZ) is approximated by $(dT/dZ) + a$, where a indicates the adiabatic lapse rate. Therefore (dT_p/dZ) indicates the equilibrium conditions. When (dT_p/dZ) is zero, it is said to be the neutral condition. If (dT_p/dZ) in a layer is negative, the layer is unstable; if it is positive, the layer is stable.

A typical environmental temperature profile (Fig. 4.8) is determined by the earth's surface characteristics, the amount of incoming solar radiation and the wind velocity. Normally temperature decreases with height. If temperature in-

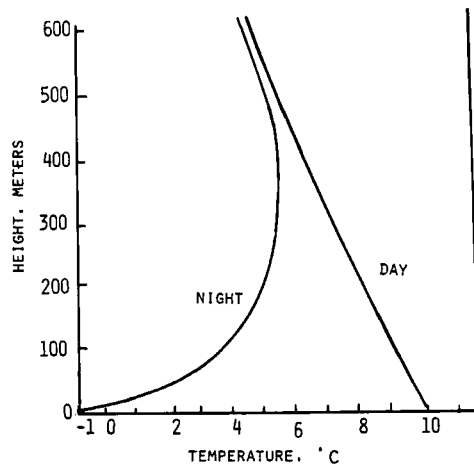


Fig. 4.8. Typical environmental temperature profiles.

creases with height at a particular location, then the area is said to be experiencing an "atmospheric temperature inversion", or simply "inversion". Nighttime inversion of the temperature profile sometimes occurs, and this is due to the absence of radiation.

As already shown in Fig. 4.7, the temperature profile controls the amount of thermal turbulence and consequently the extent of plume and puff dispersion. In addition to the thermal turbulence, fluctuations of instantaneous and average wind speed and direction are major factors in the dispersion process. Three-dimensional measurements of these fluctuations of the air are needed to determine the dispersion parameters for eqns. (22) and (23). Unfortunately, a data base of such measurements may be lacking for the area of the intended model calculation.

Instead of relying on such detailed measurements of turbulence, Pasquill¹⁰ developed a simple scheme for estimating the axial standard deviations of dispersion by classifying atmospheric stability in terms of simple and inexpensive measurements of surface wind velocity and intensity of solar radiation. Table 4.1 shows Pasquill's stability classes in which classes A through C represent the unstable condition, class D indicates neutral conditions, and classes E through F are the stable conditions. "Strong insolation" corresponds to a solar altitude greater than 60° with clear skies. "Slight insolation" means a solar altitude of 15° to 35° with clear skies. If 5/8 to 7/8 of the sky is covered with broken, middle-level clouds at the "strong insolation" level, incoming radiation is expected to reduce to the "slight insolation" level when the sky is covered with low broken clouds. Thus, solar altitude and the amount of clouds determine the daytime stability

TABLE 4.1
Stability classes¹¹⁾

Surface wind speed [m/s]	Solar Insolation (daytime)			Cloudness (night)	
	Strong	Moderate	Slight	>4/8 low cloud (thinly overcast)	<3/8 cloud
< 2	A	A-B	B		
2	A-B	B	C	E	E
4	B	B-C	C	D	D
6	C	C-D	D	D	D
> 6	C	D	D	D	D

A : Extremely unstable conditions	D : Neutral conditions
B : Moderately unstable conditions	E : Slightly stable conditions
C : Slightly unstable conditions	F : Moderately stable conditions

Turner, D.B., "Workbook of Atmospheric Dispersion Estimates", US EPA (1970)

class. The nighttime stability class is determined only by the amount of clouds.

A modified table (Table 4.2) is used in Japan in which measured solar radiation greater than 50 [$\text{cal}/(\text{cm}^2 \times \text{hr})$], between 49 and 25 [$\text{cal}/(\text{cm}^2 \times \text{hr})$] correspond with "strong insolation", "moderate insolation" and "slight insolation", respectively.

(ii) Standard deviations of plume dispersion. Fig. 4.9 shows the standard deviations of the plume dispersion, S_y and S_z , as functions of downwind distances and stability classes. These functions were derived experimentally. The experiments resulting in Pasquill's curve were performed under the following conditions: uniform terrain with the release of pollutants from near ground level and with measurements of pollutant concentrations at downwind distances of less than 1 km. Although the observations were performed at downwind distances less than 1 km from the source, the standard deviations at distances further than 1 km were estimated by extrapolation of the curve.

Briggs (1973)¹³ summarized a similar set of experiments of dispersion standard deviations done by the Brookhaven National Laboratory, the Tennessee Valley Authority and Pasquill. The sets of curves and formulas for both open-country and urban conditions were developed by interpolating these observations in order to eliminate the uncertainty of extrapolation of Pasquill's curves.

If measurements of turbulence are available, then it is preferable to estimate the standard deviations of the plume dispersion from the standard deviations of wind direction fluctuations. Despite the recommendation by Hanna et al (1977)¹⁴ to use turbulence measurements for estimating the standard

TABLE 4.2

Modified table of stability classes used in Japan¹²⁾

Surface wind speed at 10m [m/s]	Day Solar Radiation [$\text{cal}/\text{cm}^2 \text{ hr}$]			Day and Night Cloud Amount	Night Cloud Amount	
	> 50	49-25	< 24		5-10	0-4
< 2	A	A-B	B	D	G	G
2-3	A-B	B	C	D	E	E
3-4	B	B-C	C	D	D	D
4-6	C	C-D	D	D	D	D
6 <	C	D	D	D	D	D

A : Extremely unstable conditions
 B : Moderately unstable conditions
 C : Slightly unstable conditions
 D : Neutral conditions

E : Slightly stable conditions
 F : Moderately stable conditions
 G : Extremely stable conditions

deviation of the plume dispersion, Pasquill's curve is still popular because it is easy to use.

Under calm conditions, the axial standard deviation of the puff dispersion model is not a function of the downwind distance, but rather a function of the time elapsed since a puff release. The standard deviations are assumed to be proportional to the elapsed time t [sec];

$$s_x = s_y = \alpha * y \quad (27)$$

$$s_z = \gamma * y \quad (28)$$

The proportional constants, α and γ , are empirically determined according to the stability classes (Table 4.3).

(iii) Effective plume height. The effective plume height is the sum of stack height and estimated plume rise. This is an important factor in determining the maximum pollutant concentration at ground level where most people breathe. Plume rise occurs due to the upward momentum of the stack effluent at the outlet and the upward force of buoyancy. The initial upward movement of the stack effluent is governed by the forces of momentum and friction. The buoyancy force operates continuously on the plume until it is at equilibrium with its surroundings; therefore, the plume rise also depends on the atmospheric stability and the surrounding mean wind velocity.

There are numerous formulas for predicting plume rise based on empirical and/or theoretical considerations. The functional form of the theoretical equations, whose coefficients come from experimental data, are derived from the

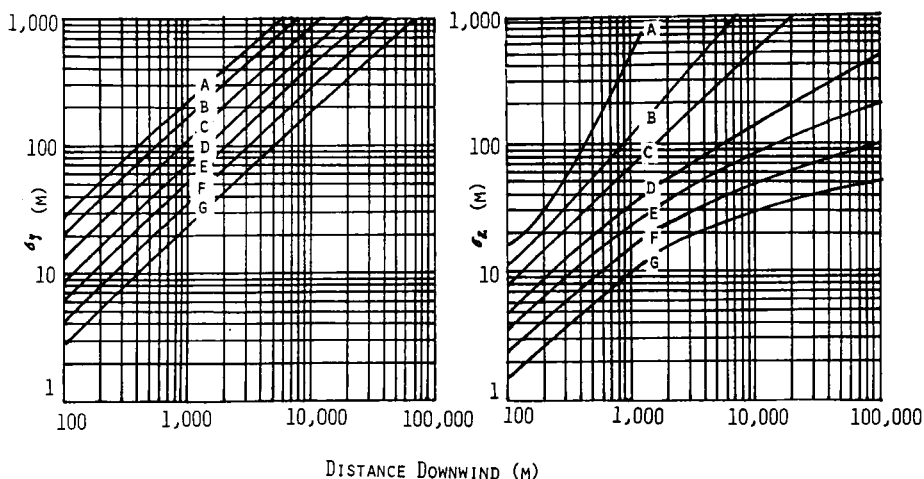


Fig. 4.9. Horizontal and vertical dispersion standard deviations as function of downwind distance from source by Gifford (1961).¹²

conservational laws of heat and momentum. However, atmospheric motion is too complex to include all of the variables which may affect the plume rise in the rather simple model equations. Empirical equations can be more accurate than the theoretical equations for specific conditions. When empirical models are applied to different conditions, some parameters may need to be adjusted. The most popular plume rise equations are after Moses and Kraimer (1972) and found in their textbook⁹.

Earlier work predicting plume rise was performed by Holland (1953), whose formula included two terms concerning the momentum and the buoyancy forces. Various studies have indicated that this equation underestimates the plume rise by a factor of 2 or 3.

Morse and Carson developed the empirical equation accounting for atmospheric stability, in which the effect of buoyancy was expressed by the square root of the heat emission rate.

Briggs plume rise equations classified by heat emission rate and potential temperature gradient are currently used in many applications.

(iv) Vertical profile of wind speed over the earth's surface. Surface wind velocity is usually measured at 15 m above the ground in Japan, a height lower than the typical stack height. A wind velocity profile in the atmospheric surface layer should be examined to obtain the proper mean wind velocity for use in the dispersion models. Wind velocity generally increases with elevation due to the highly variable frictional effects of the earth's rough surface. Three equations for predicting the wind velocity at a specific height will be discussed. The first two are based on physical phenomena and the third is

TABLE 4.3
Dispersion parameters for puff equation¹²⁾

Stability class	Wind speed			
	0.4 [m/s]		0.5-0.9 [m/s]	
	$\sigma_x = \sigma_y = \alpha t$		$\sigma_z = \gamma t$	
	α	γ	α	γ
A	0.948	1.569	0.748	1.569
A-B	0.859	0.862	0.659	0.862
B	0.781	0.474	0.581	0.474
B-C	0.702	0.314	0.502	0.314
C	0.635	0.208	0.435	0.208
C-D	0.542	0.153	0.342	0.153
D	0.470	0.113	0.270	0.113
E	0.439	0.067	0.239	0.067
F	0.439	0.048	0.239	0.048
G	0.439	0.029	0.239	0.029

empirically drawn.

If a constant shear stress with elevation is assumed, then the mean wind velocity profile in the surface layer of several tens of meters is:

$$U = (U_o/k) \ln(Z/Z_o) \quad (29)$$

Here, k is the Karman constant ($k = 0.4$). The friction velocity, U_o , is related to the surface shear stress (S_o) and air density (ρ) as follows:

$$U_o = (S_o/\rho)^{1/2} \quad (30)$$

U_o is usually determined from the wind velocity profile.

This logarithmic velocity profile formula should be used only for neutral stability conditions, while for non-neutral stability conditions a log-linear form is given:

$$U = (U_o/k) (\ln(Z/Z_o) + a * Z/L) \quad (31)$$

The Monin-Obukhov stability length, L , is a function of heat transfer rate at the surface, which is difficult to obtain.

Therefore, the power law velocity profile equation, which is empirically derived, is used in many cases.

$$U = U_1 * (Z/Z_1)^p \quad (32)$$

where U_1 is the observed wind velocity at a height Z_1 . Values of exponent p ranges from 0.1 to 0.3 relating to the stability classes.¹²

4.4 ESTIMATION OF EMISSION

Air pollutants found in the atmosphere are discharged from a variety of different sources. These include natural processes and human activities. Emissions produced by human activities are the principal contributors to pollution in urban and suburban areas. The contributions to air pollution from these sources are generally placed in two categories: stationary sources and mobile sources.

4.4.1 Stationary sources

The time averaged emissions, from stationary sources identified with a plant or an installation fixed at a certain location, are primarily from fuel combustion, industrial processes and solid waste disposal.

Combustion fuels include petroleum oils (heavy oil, light oil, kerosene and naphtha), coal, coke, natural gas, liquid petroleum gas and wood. The industrial processes include metals smelting, petroleum refining, mineral products processing and chemical processes. The solid waste disposal processes

include incineration and agricultural burning. Organic solvent evaporation from painting, gasoline retailing and residential combustion from cooking and heating are miscellaneous sources.

The emission sources are identified as point sources and area sources depending on their physical scale. Point sources are often large, single sources of pollutants emitted from the tall stacks of power plants for example. Area sources, which are treated differently from point sources in model calculations because of their scale, however, contribute substantially to air pollution in urban and suburban areas. These area sources are numerous small industries, commercial buildings and residences.

Sulfur oxides, nitrogen oxides, carbon monoxide, hydrocarbon compounds and particulate matter are considered primary pollutant species from these sources. In addition, toxic substances such as hydrogen chloride and mercury vapor, which are sometimes found due to waste incineration processes, are included as air pollutants.

Sulfur oxides are released into the atmosphere by the oxidation of sulfur in coal or other fuels during combustion processes such as electric power generation, smelting of sulfur bearing ores, use and manufacturing of sulfuric acid, paper production, waste disposal processes, etc. Sulfur dioxide is the primary component of the sulfur oxides. It is emitted mainly from liquid and solid fuel combustion. Emissions can be estimated using the mass balance equation and assuming that the sulfur in the fuel is converted to SO_2 . The accuracy of the estimate depends on the accuracy of the fuel sulfur content determination and on the fuel consumption rate. The sulfur content of coal and crude oil varies widely from approximately 0.1% to 7%, according to the geological source of the fuel. Sulfur content also varies in each distilled fraction of crude oil. Heavier crude oil fractions contain more sulfur. Japanese standards for sulfur content in heavy oil and kerosene are listed in Table 4.4. Pre-treatment to remove sulfur is required to meet the standards. The average sulfur content of crude oil imported into Japan was 1.4% in 1983. The capacity for pre-treatment of heavy oil was about 80 million cubic meters, adequate for the domestic heavy oil consumption. In model calculations, the stack gas removal of sulfur dioxide is also taken into account. The 1983 removal capacity of SO_2 was $140 \times 10^6 \text{ Nm}^3/\text{hr}$ for about 1400 air pollution control devices.

Stationary sources of carbon monoxide emission in urban areas are normally quite small in comparison with transportation sources. Combustion with insufficient oxygen which sometimes occurs in cooking and heating by city gas or charcoal can produce large amounts of carbon monoxide.

Nitrogen oxides, including nitric oxide (NO) and nitrogen dioxide (NO_2), are emitted from fuel combustion, production and use of nitric acid, explosives

production and other industrial processes. Formation of nitrogen oxides in a combustion process is more complicated than formation of sulfur oxides because they are produced from nitrogen gas in the air as well as from nitrogen compounds in the fuel. The rate of formation of nitrogen oxides derived from atmospheric nitrogen, sometimes called thermal NO_x , is primarily influenced by the flame temperature. Thermal NO_x production may be determined from the ratio of fuel to air, fuel type and the burner type. Estimation of nitrogen oxides emission based on the fuel consumption rate is therefore less accurate than that of sulfur oxides. Specific operating conditions of appliances as well as fuel consumption rates are required to estimate NO_x emission. Ambient NO_x is usually considered to be conserved in the model calculations, but the ratio of NO_2 to NO_x is variable. Nitric oxide is primarily produced at the point of combustion and discharged from a source. In the atmosphere, nitric oxide is photochemically oxidized to nitrogen dioxide, a strong oxidant which is considered to cause adverse health effects. Because ambient nitrogen dioxide concentrations are the subject of air quality standards in Japan and other countries, the environmental nitrogen dioxide concentration should be estimated by the air quality models. The methods used to evaluate photochemically produced nitrogen dioxide will be discussed in the following section.

Emissions of volatile hydrocarbons from stationary sources are caused by evaporation from storage areas, by solvent extraction processes, and by consumer gasoline distribution, etc. Hydrocarbon emissions from combustion are normally quite small because of the almost complete combustion of the fuel.

Particulate emission from stationary sources results from combustion processes, grinding operations and from other minor processes. Emission rates of combustion particles vary widely depending on fuel type, ash content of the fuel, temperature of the combustion, air flow rate to the combustion and humidity as well as combustion equipment conditions. These emissions can be

TABLE 4.4

Japanese standards for fuel sulfur content

	Class	Sulfur content (wt%)
Kerosene	1	< 0.015
	2	< 0.50
Heavy oil	A	< 2.0
	B	< 3.0
	C	< 3.5

largely eliminated if adequate controlling techniques are applied, such as, cyclones, filters, electrostatic precipitators and wet scrubbers. Emissions from non-combustion processes are produced by chemical manufacturing, petroleum refining, metal processing, etc. Particulate formation by atmospheric reactions is also important in evaluating acid deposition, and so on.

Size distribution and chemical composition of particulate matter are essential in assessing the human health impact. Among the effects on the respiratory system are gross toxicity from heavy metals, carcinogenesis from organics and direct damage by deposition of granular and corrosive materials. The deposition efficiency of particulates in the pulmonary system varies with particle size. As the particle size decreases, particles are more likely to reach the pulmonary region and remain in the lungs; therefore the fraction of fine particles should be monitored to evaluate health effects. In Japan, the mass concentration of suspended particulate matter of diameter less than $10\text{ }\mu\text{m}$ is measured.

It is unrealistic to measure the actual emissions from all air pollution sources. Emission rate estimates, are generally based on fuel consumption rates and/or production rates which are validated by on-the-spot inspections. This is a practical means of compiling an emission inventory. The first step in constructing the emission inventory is to collect basic information from all sources. The basic information consists of five items: 1) identification of a particular factory; 2) information on the manufacturing processes; 3) air pollution control equipment; 4) range of operating conditions; and 5) smoke and air pollutant emissions at the operating conditions.

The factory identification includes name, address, telephone number, category of the factory and name of the person responsible for air pollution control. The information on the manufacturing process includes the process name, product name, and characteristics of the fuel, burners and stacks. Fuel information for each facility includes the type and amounts used per year, and the contents of sulfur, nitrogen and ash. As for burners and stacks, the type and rating size of burners, and the height and location of stacks are reported as well as the capacity and efficiency of pollution control equipment and the name and type of device (i. e. electrostatic precipitator, scrubber, fabric filter, etc.) Operating conditions include typical production rates, fuel consumption rates and operation periods and schedules of the facilities. The emission rate of smoke, its temperature and oxygen content as well as the emission rate of NO_x , SO_x and dust are reported.

After collecting these data in the area of interest, on-the-spot inspections are required to confirm their accuracy. It is desirable to do the on-the-spot inspection on all of the large scale sources, while for the area sources, a certain percentage of facilities should be the subject of inspection. Emission

factors of pollutants from various types of fuel and facilities can be obtained based on the basic information and on-the-spot inspection data.

The emission inventory of the region is compiled using the emission factors, fuel consumption rate and production rate. If the pollutant concentration data at the outlet of the stack are available, the emission rate is calculated by:

$$\begin{aligned} \text{Emission rate [kg/hr]} &= \text{pollutant concentration [ppm]} \\ &\times \text{dry gas discharging rate [Nm}^3\text{/hr]} \\ &\times \text{molecular weight [g]} \times (1/22.4) \times 10^{-6} \end{aligned} \quad (33)$$

When the emission factors are used, the emission rate is:

$$\begin{aligned} \text{Emission rate [kg/hr]} &= \text{emission factor [kg/kcal]} \\ &\times \text{fuel consumption rate [kg/hr]} \\ &\times \text{calorific value [kcal/kg]} \end{aligned} \quad (34)$$

For sulfur oxides emission, the sulfur content of the fuel instead of the emission factor can be used for the emission rate calculation:

$$\begin{aligned} \text{Emission rate [kg/hr]} &= \text{fuel consumption rate [kg/hr]} \\ &\times \text{sulfur content [wt\%]} \times 10^{-2} \end{aligned} \quad (35)$$

4.4.2 Mobile sources

Transportation, on land, sea, and in the air, contributes air pollution burdens which match stationary source emissions. The principal pollutants emitted during transportation are carbon monoxide, nitrogen oxides, sulfur oxides, hydrocarbons and particulate matter. Metal aerosols originate from fuel treatment additives, such as lead, and fuel impurities. Discussion here will focus on vehicle emissions which account for a large fraction of urban air pollutants. The magnitude of vehicle emissions is estimated by constructing an emission inventory using emission factors and traffic flow volumes in a specific region.

(i) Traffic flow. Vehicle emission factor differ with vehicle class, so the traffic flow must be measured for each class. The Japanese Ministry of Construction uses 8 vehicle categories in standard road traffic surveys:

1) light passenger car; 2) passenger car; 3) bus; 4) light truck; 5) compact truck; 6) freight-passenger car; 7) heavy duty truck; and 8) special purpose vehicle.

These 8 classes are sometimes collapsed into 6 classes by combining classes 4 and 5, and classes 7 and 8.

In model calculations, highways and intercity roads, where traffic volumes are usually large and vehicle speed is relatively high, are treated as line sources of air pollutants, while community roads within cities and towns are considered to be area sources.

The traffic flow volume can be measured or estimated in various ways. The most accurate but labor intensive way is to count the number of vehicles

passing a specific location mechanically or manually. Appropriate counting intervals are needed to reliably measure diurnal, weekly and seasonal average traffic flows. However, it is not realistic to observe traffic flow on all roads in the region of interest. The alternative is to estimate traffic flow from at least two aerial photographs which are taken at specific intervals. The aerial photographic resolution should be adequate to identify vehicle classes. We have to be careful not to count parked vehicles which sometimes comprise more than 80% of the vehicles in the urban aerial photographs.

Traffic flow on community roads can be estimated from socio-economic parameters, such as type of land use, and population and road density. Toll tickets may be used for counting traffic on toll roads, tunnels and bridges.

Using these methods, traffic flow is obtained in the units of (number of vehicles x km/hr). For the line sources such as highways and intercity roads, traffic flow is calculated from direct observation:

$$\text{Traffic flow} = [\text{number of vehicles per hour}] \times [\text{length of road}] \quad (36)$$

and from the air photograph:

$$\text{Traffic flow} = [\text{number of vehicles per 1 km of road}] \times [\text{driving speed}] \times [\text{length of road}] \quad (37)$$

For the area sources, traffic flow on community roads is calculated from the following equations based on the aerial photographs.

$$\text{Traffic flow} = [\text{number of moving vehicles per area}] \times [\text{area}] \times [\text{driving speed}] \quad (38)$$

The driving speed is calculated from the two aerial photographs taken at specific intervals.

(ii) Emission factors.

(ii-1) Regulations. Since automobile exhaust was identified as the major source of air pollution in urban and suburban areas, the regulation of exhaust gas has proceeded by encouraging technological developments. As the emission standards were intensified, so pollutant emissions from automobiles varied with their model year. In the early days of the regulation beginning in 1961 in California, simple, low cost technology was applied, for example, crankcase emission controls. Emission standards for exhaust gases were first enacted in 1966 in the U.S.A. and in Japan. Only hydrocarbons and carbon monoxide were regulated. The control of nitrogen dioxide, which required more technological development, started in 1971 in the U.S.A. and in 1973 in Japan. In Japan, NO_x emissions of 1978 model passenger cars were reduced by 90% of their 1973 levels.

The emission standards are prescribed for specific test cycle modes which must reflect the actual emissions. Emissions vary considerably with different

driving conditions, that is, long or short trips, stop and go driving in urban traffic and high speed traveling on highways, etc. It is almost impossible to include all of the driving conditions in the emission tests. The standard test cycle modes were developed to represent the typical traffic patterns in urban areas where automobile exhaust is a major source of air pollution.

A 10-mode test cycle used in Japan represents a daytime traffic pattern in urban areas. Distance traveled per test cycle is 0.664 km and average driving speed is 17.7 km/hr. After warming up the engine, the NO_x emission test is performed on a dynamometer according to the 10 mode test cycle. Since 1975, an 11-mode test cycle which simulates commuter traffic conditions from a suburban area to the town center was added to the NO_x emission test. As it simulates early morning or late evening driving conditions, the 11-mode test is done without warming up the engine.

(ii-2) Typical driving pattern. As the 10-mode and 11-mode test cycles were developed for regulatory purposes, they do not always represent the typical traffic pattern in a specific region. Although the easiest way to do the emission inventory is to use the 10-mode or 11-mode test cycles as representative of the driving pattern in the area of interest, it is often necessary to approximate the typical driving patterns in the region for the model calculations.

The steps used to determine the typical traffic pattern are as follows:

- 1) Select the representative roads in the region by road type, number of traffic lanes, traffic flow volume, etc. as criteria.
- 2) Decide the observation times, that is, on weekdays and weekends at peak and off-peak times, and so on.
- 3) Drive a test car equipped with a driving pattern analyzer which can record driving speed, driving modes (gearbox position), brake operation, engine rpm, etc.
- 4) Analyze the observed driving pattern data to determine the typical driving patterns. Extraction of the typical driving patterns is performed by classifying the data according to: a) time fraction of idling, acceleration, deceleration, and constant speed periods, b) acceleration, deceleration, and constant speed, c) trip length and number of modes between idlings, and d) average speed.

Fig. 4.10 shows examples of the typical traffic patterns found on various types of roads in urban areas.

(ii-3) Measurement of emission. Once the typical driving pattern is determined, emission rates of pollutants for the driving pattern can be measured in laboratories using the dynamometer. Test cars should be selected to reflect the chronological changes in emission standards.

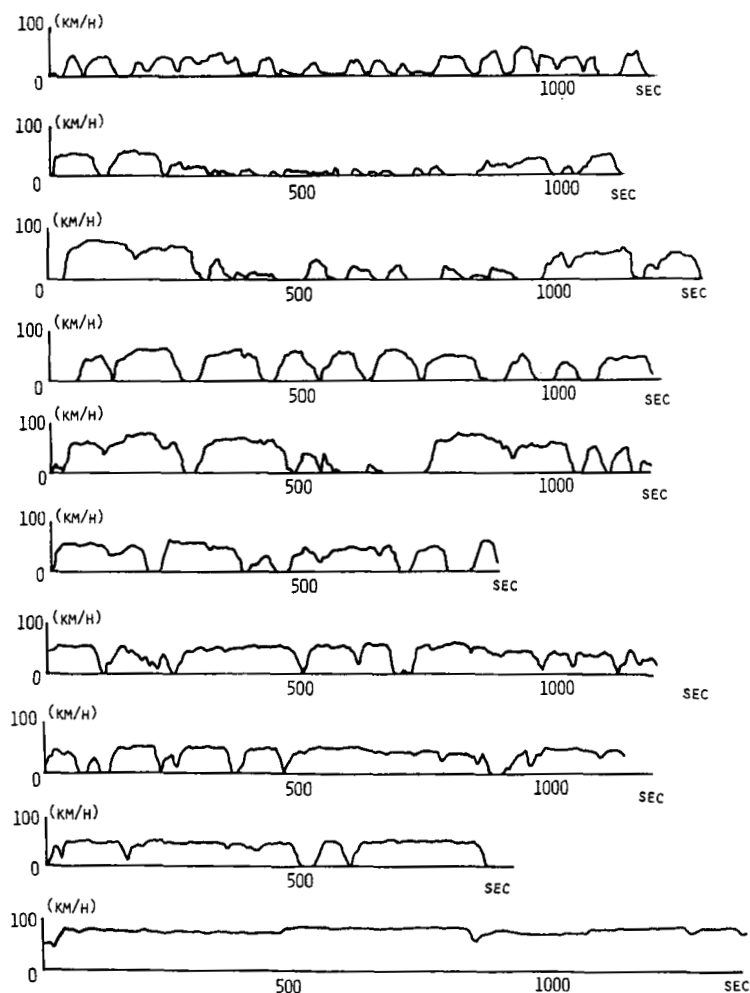


Fig. 4.10. Examples of driving patterns in urban area.

4.5 EXAMPLE OF COMPUTER SIMULATION

4.5.1 Subject of simulation

In the former sections, I briefly described the sub-models composing the simulation for reproducing the present environmental conditions or for predicting the future trend. In this section, I will show an example of the simulation for ambient NO_2 concentrations.¹⁶ A project team was set up by local government including experts from universities, research institutes and local government departments. They developed a simulation model which could reproduce the NO_2 concentration profile of the basic year (1978) and then use

the model to predict the future NO_2 profile through 1985 by entering the predicted emission rates of nitrogen oxides.

The study region for this simulation is about $3,800 \text{ km}^2$, located north of Tokyo. The central and eastern parts of the region comprise two-thirds of the total area and is flat land while the western part is hilly. The southeast area has a high population density. There are about 5,000 facilities emitting smoke and the total road length is 47,000 km. There are about 1.6 million vehicles registered in the region or almost one per family.

Ambient NO and NO_2 concentrations are continuously monitored at 50 observation stations over the entire region and 9 additional stations are located along roads. Yearly averages of NO_2 and NO_x concentrations over the past 5 years was almost constant at about 23 ppb in the south and 18 ppb in the north.

Although ambient NO_2 concentrations were the primary subject of this study, the NO_x profile was modeled first, followed by the NO_2 simulation. Nitrogen dioxide is not considered to be a conserved component due to its formation from NO by photochemical reactions, while NO_x is assumed to be conserved in the simulation.

4.5.2 Input data

(i) Meteorological data. The initial year of the simulation was 1978. The fractional distribution of the wind direction, monthly averages of wind velocity and temperatures of the initial year were collected together with the averages for the past decade. We can conclude from these observations that the

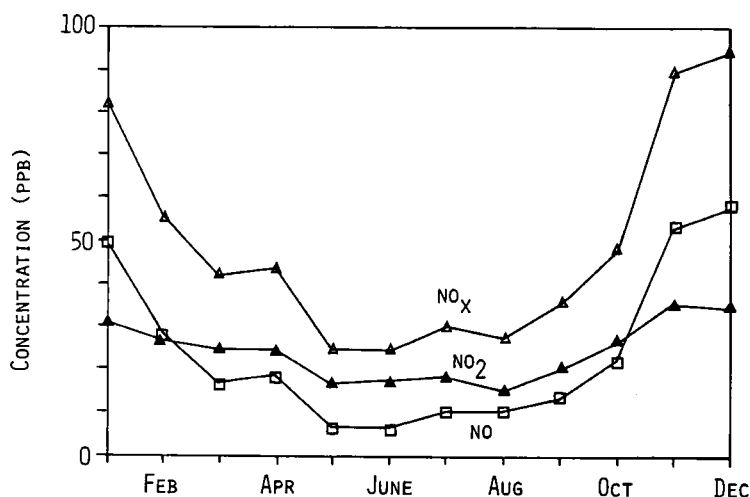


Fig. 4.11. Seasonal variations of observed nitrogen oxides concentrations.

initial year was not a meteorologically extraordinary year.

Frequency distributions of the stability classes were calculated from the meteorological data at 34 observation stations in the region. About half the meteorological conditions belong to stability class D (neutral condition), while G (very stable condition) is the second highest frequency class. According to the vertical gradients of potential temperature, nighttime was usually more stable than daytime, and wintertime was more stable than summertime. The observed vertical gradients of potential temperature lead to the high ambient NO_2 and NO_x concentrations in the wintertime as shown in Fig. 4.11.

Mean wind velocity in the upper layer was estimated based on the power law.

(ii) Source emission data. An inventory of NO_x emissions from stationary sources was made using measurements of stack gas and calculated emissions. Data was collected from more than 5,000 facilities in the region. The following equations were used to calculate NO_x emissions:

Waste disposal process:

$$\text{Emission (kg/yr)} = \text{amount of waste (ton/yr)} \times \text{emission (1.04 kg/ton)}$$

Cupola furnace:

$$\text{Emission (kg/yr)} = \text{coke consumption (kg/yr)} \times \text{calorific value (kcal/kg)} \times \text{emission factor (4.31 kg/kcal)}$$

Electric arc furnace:

$$\text{Emission (kg/yr)} = \text{production (ton/yr)} \times \text{emission factor (0.779 kg/ton)}$$

Other facilities:

$$\text{Emission (kg/yr)} = \text{fuel consumption} \times \text{calorific value} \times \text{emission factor}$$

Total NO_x emissions from the stationary sources were about 18,000 ton/yr. NO_x emission from cement kilns located in the western part of the region accounts for over half the total emission of the stationary sources.

The NO_x emission inventory of mobile sources was prepared using the following procedures. Traffic flow, on highways or intercity roads, was obtained from observations of each road. Traffic flow on community roads was estimated by the following equation:

$$Y = 81.215 X_1 + 309.812 X_2 + 5.171 X_3 + 94.803 X_4 - 2.590 X_5 + 441.281 \quad (R = 0.817)$$

where:

Y (number of cars $\times$ km/12h) = Estimated traffic flow

X_1 :(km²) = Square of road length of width between 2.5 and 5.5 m

$X2:(km^2)$ = Square of road length of width between 5.5 m and 11.0 m

$X3:$ = Square root of population

$X4:$ = Number of manufacturing facilities

$X5:$ = Number of service facilities

This equation was derived from the aerial photography and the observations of traffic flow in some areas in the region.

NO_x emission factors for the various classes of vehicles at various driving speeds were obtained from the dynamometer test. The car age distribution was taken into account. Since the emission factors change with the driving speed, the average driving speeds on the highways were calculated by:

$$V = 0.741 \times V_m + 979 \times (WIDE/Q) + 6.61 \times (1/CROS) - 4.94 \times TP1 - 2.70 \times TP2 - 13.8 \quad (R = 0.841)$$

where:

$V(km/h)$ = average driving speed

$V_m(km/h)$ = regulated driving speed

$WIDE/Q(m \times h/\#)$ = reciprocal of traffic density
= (road width (m)/traffic flow rate (#/h))

$1/CROS(km/\#)$ = reciprocal of traffic light density

$TP1$ = dummy variable

$TP2$ = dummy variable

(in the evening peak, $TP2 = 2$, otherwise $TP2 = 0$)

For the community roads, average driving speeds were estimated separately by type of area, for example, 17 km/hr in the business area and 43 km/hr for farmland. The total NO_x emission from all mobile sources was about 42,000 ton/y of which highways and intercity roads contributed 73%. The areas highly polluted by mobile source emissions were in the southeast and along the highways and intercity roads (Fig. 4.12).

The NO_x emission from miscellaneous sources such as gas stoves and space heaters in residences was also estimated from the fuel consumption and corresponded to 2.5% of the total NO_x emission.

The effective heights of the emission sources were estimated. For a high stack, the Morses & Carson's equation was used for windy conditions and the Brigg's equation was used for calm conditions. For the lower stacks, typical heights were used. Release heights of mobile exhaust for windy conditions were assumed to be the road height for highways and 3 m for community roads. For calm conditions, they were assumed to be 4 m for community roads and the road height plus 3 m for highways.

4.5.3 Calculations

The plume and puff equations were used for windy (>0.4 m/s) and calm (<0.4

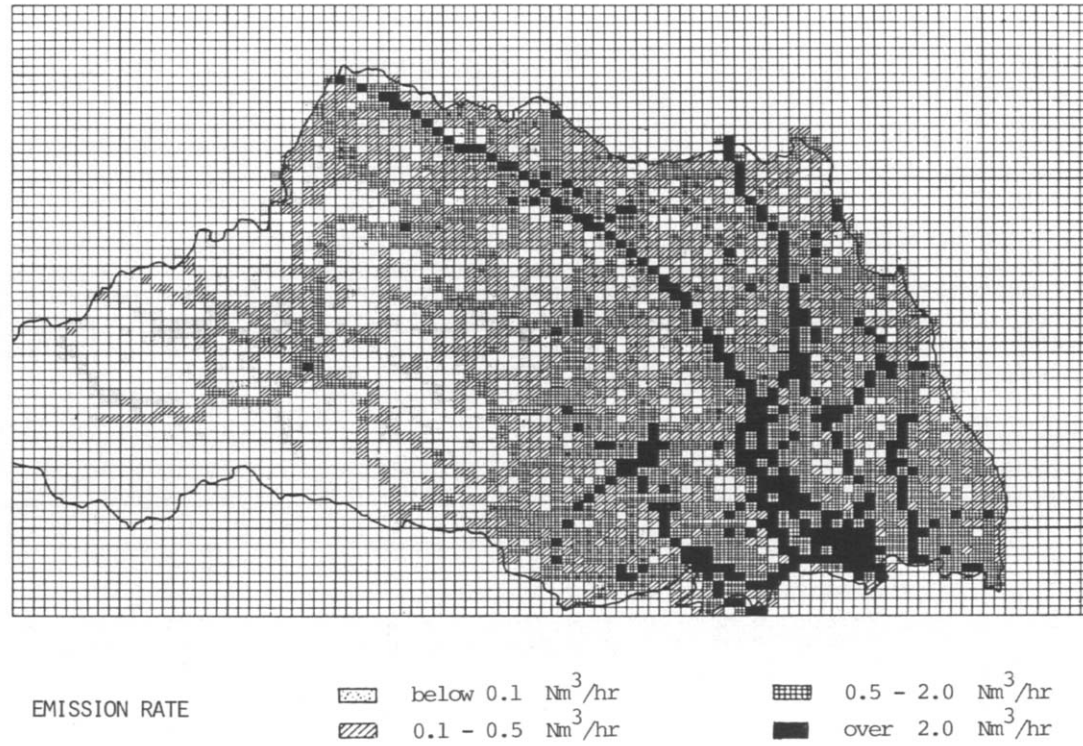


Fig. 4.12. An example of spatial distribution of NO_x emission from automobiles in a suburb of Tokyo.¹⁶

m/s) conditions. Stationary sources were classified according to their stack height point sources (stack higher than 20 m) and area sources (stack lower than 20 m). Mobile emissions from highways and intercity roads, and from community roads are considered line sources and area sources, respectively. Miscellaneous sources are treated as area sources.

Spatial and temporal scales of the calculation were determined by population density and temporal variation of ambient NO_2 concentrations. The study region, which is about 70 km from east to west and 60 km from north to south, was divided into 1 km squares in high population density areas and 2 km squares in rural areas. The total number of cells was 2076. Eight different time categories were set up and a yearly average was obtained from weighted averages of these time categories. The eight time categories consisted of 2 seasons with 4 periods in each day: winter (December through March) and summer (April through November), with morning, daytime, evening, and nighttime.

NO_x concentrations were calculated using a simulation model and the corresponding NO_2 concentrations were predicted by the following equation based on the calculated NO_x concentrations:

$$\text{NO}_2 = \text{NO}_x * (1 - a * (\exp(-kt) + b)/(1 + b))$$

where, a is the ratio of NO to NO_x at a release point ($a = 0.85$ in this case) and b is a suppression factor of NO oxidation to NO_2 , which depends on the intensity of sunlight and the ozone concentration. In this case, b varies with

TABLE 4.5

Criteria for validation of simulation¹²⁾

Rank of accuracy	Criteria
A	$A_0 < \{(1/3)(Y - B_g) + B_g\}$, $P = (0.8-1.2)$, $r > (0.71)$, $S'/Y < (1/4)$ or $A_0 < \{(1/3)(Y - B_g) + B_g\}$, $S'/Y < (1/5)$
B	$A_0 < \{(2/5)(Y - B_g) + B_g\}$, $S'/Y < (1/4)$
C	$A_0 < \{(2/5)(Y - B_g) + B_g\}$, $S'/Y < (1/3)$

$A_0 = (Y - X)$; Y = average of observed concentrations; $Y(i)$ = observed conc. at i -th location; X = average of calculated conc.; $X(i)$ = calculated conc. at i -th location; P = regression coefficient of observed on calculated conc.; r = correlation coefficient; $S' = \sqrt{\{Y(i) - A_0 + X(i)\}^2 / (n-2)}$; B_g = back ground concentration (in this case $B_g(\text{NO}_2) = 0.002$ ppm, $B_g(\text{NO}_x) = 0.003$ ppm)

the time period of the calculation ranging from 0.3 to 0.55. The exponent, k , indicates the overall reaction rate of NO oxidation, which differs for different emission sources as follows:

$$\begin{aligned} k &= 0.00618 \times U \times (O_3) : \text{stationary point source} \\ &= 0.0618 \times U \times (O_3) : \text{stationary area source} \\ &= 0.100 \times U \times (O_3) : \text{mobile, miscellaneous source} \end{aligned}$$

where U (m/s) and (O_3) (ppm) are the average wind velocities and the background ozone concentrations.

The simulation was validated by comparing observed and predicted NO_x concentrations. The validation criteria are: 1) difference between observed and predicted average concentrations; 2) correlation coefficient between them; 3) regression coefficient of the predicted concentrations compared to the observed concentrations; and 4) the standard error of the predicted concentrations from the regression line where the regression coefficient is fixed at 1.0. The precision of the prediction is evaluated by 3 ranks according to the criteria (Table 4.5). Precision rank A is required for the yearly average concentration and rank C for the 8 time categories (Table 4.6).

The simulation of the ambient NO_x and NO_2 concentrations was highly accurate in all of the time categories. For example, yearly averages of predicted concentrations and observed concentrations at 34 stations in the region agreed well as shown in Fig. 4.13. The spatial distribution of the predicted yearly average of NO_2 concentration is shown in Fig. 4.14, in which high NO_2 concentration areas were found in the southeast, and polluted lines tended to be in the northwest. This suggested that automobile traffic was a major source of NO_2 pollution in this region as clearly shown in Fig. 4.12.

4.5.4 Prediction of future NO_2 concentrations

Since the simulation satisfactorily reproduced ambient NO_2 concentrations in 1978, future NO_2 concentrations can be predicted by entering estimated source emission data into the model.

TABLE 4.6

Desirable rank to be achieved by simulation at each time categories¹²⁾

	Summer	Winter	Yearly average
6 am - 10 am	C	C	B
10 am - 4 pm	C	C	B
4 pm - 9 pm	C	C	B
9 pm - 6 am	C	C	B
Daily average	B	B	A

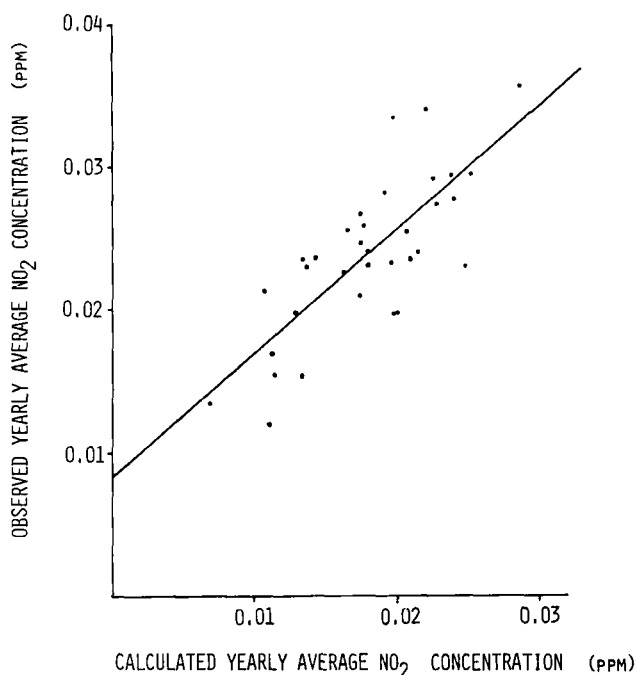


Fig. 4.13. Correlation of calculated and observed NO₂ concentrations¹⁶.

NO_x emissions from stationary sources were estimated as follows. Emissions from major facilities were assessed from an industrial questionnaire polling their production plans. For minor enterprises, which were treated as area sources, estimated production growth rates for each business category or projected population growth in the region were used to predict future emission changes. Development plans for new industrial parks were also taken into account. The calculations indicated that NO_x emissions from stationary sources in 1985 were expected to increase by 33% over 1978 levels from 18 Kton/yr to 24 Kton/yr.

Estimates of mobile source emissions were composed of the predicted traffic flows on existing and planned roads. Emission factors were modified allowing for changes in age distribution of vehicles and chronological change of exhaust gas regulation. About 250 km of additional highways and community roads were planned to be in use by 1985. The traffic flow used in the 1978 simulation was re-allocated to the existing and planned roads by assuming that all the planned roads would be open for traffic during the target year. Growth rates of traffic flow were estimated by comparing the traffic flow in 1977 and 1980. Since the maximum capacity of traffic flow is physically limited, the growth

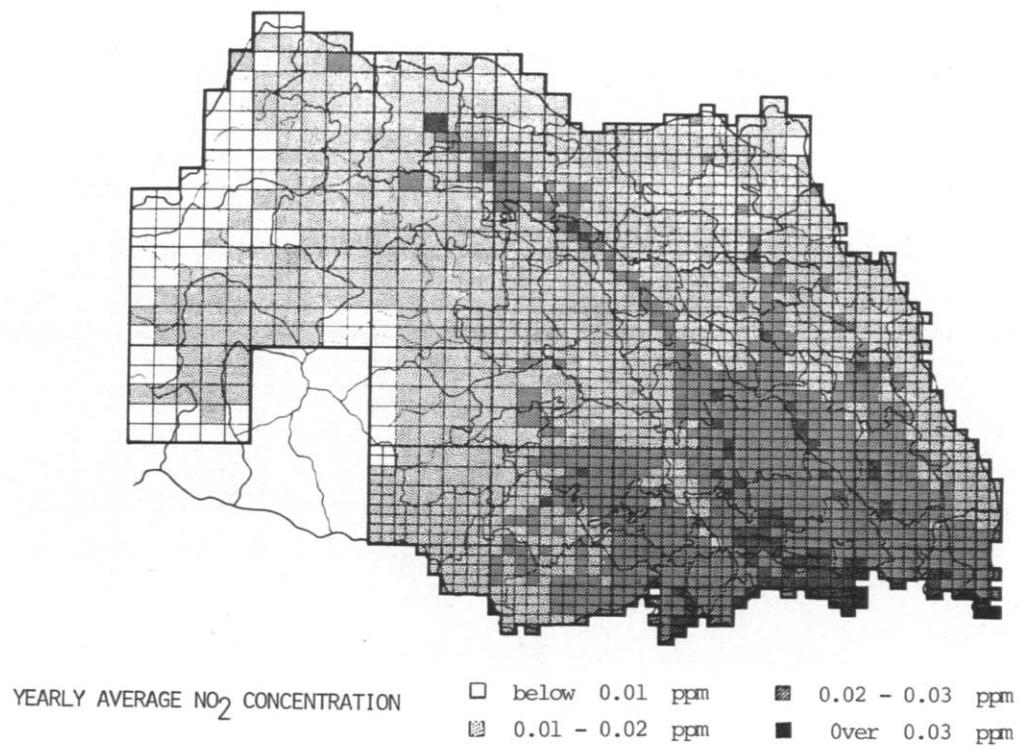


Fig. 4.14. An example of calculated NO₂ concentration distribution in a suburb of Tokyo¹⁶.

rate of traffic flow on each road varies with the extent of traffic jams. When the extent of traffic jams was less than 1, the traffic flow on an existing road might increase by about 5% yearly. However, if the extent exceeded 1.8, it was assumed the traffic flow could not increase any more. The expected increase of traffic flow during the 7 years prior to 1985 was calculated for each road by applying the growth rates. The traffic flow was projected to increase by 30% from 43×10^6 (vehicle x km)/day (1978) to 56×10^6 (vehicle x km)/day (1985).

The age distribution of vehicles is estimated by the survival curve of vehicles in the region. Vehicle registration data was used to obtain the survival curve but the data for vehicles over 10 years old was not available, so the lifetime of all kinds of vehicles was assumed to be 13 years.

NO_x emissions from mobile sources in the region were calculated based on the estimation of the traffic flow, the age distribution of vehicles, and regulatory standards for exhaust gases. Despite an expected increase in the traffic flow of 30% over 7 years, the NO_x emissions in the region were

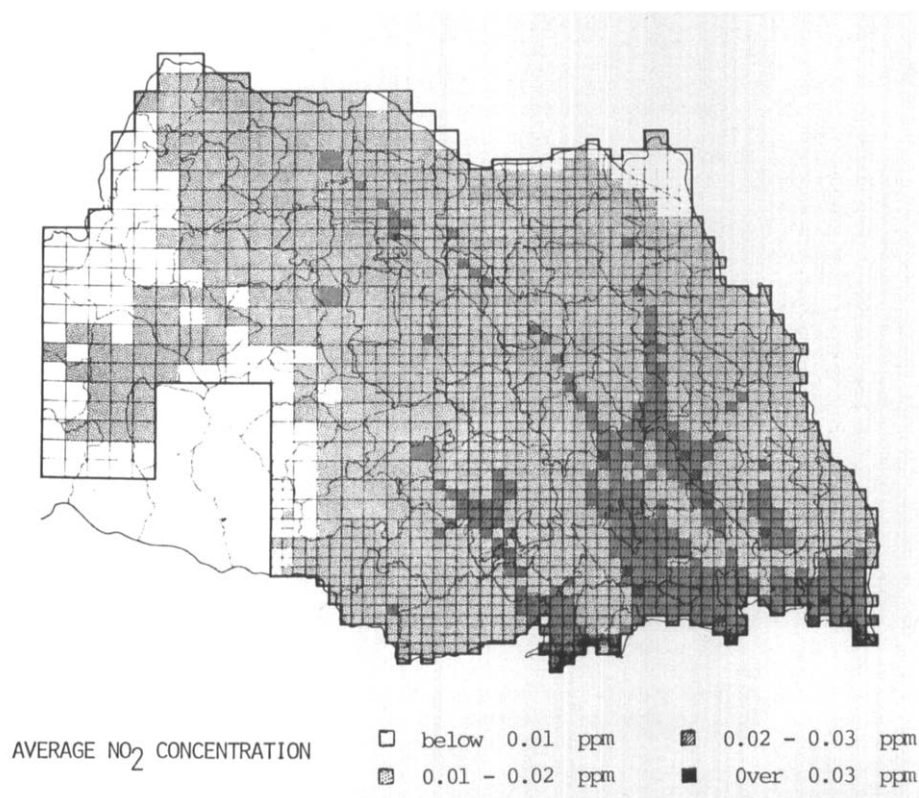


Fig. 4.15. NO_2 concentration predicted from estimated emission¹⁶.

predicted to decrease by 24% due to the replacement of old vehicles with stringently regulated vehicles.

Total NO_x emission would be reduced by implementation of the regulations, but some areas which are along the heavily traveled roads or at the southeast edge of the region, would not achieve the NO_2 ambient air quality standard. (Fig. 4.15). There are 11 cells out of the 2076 of the simulation, where NO_2 concentrations are expected to exceed 30 ppb for the yearly average concentration. Feasible alternatives for reducing NO_x pollution to meet the air quality standard all over the region are still needed. If we can make a 50% reduction of mobile source emissions, the yearly average of NO_2 concentration in all of these cells would be lower than 30 ppb. A combined reduction by 40% of mobile source emissions and 50% of stationary source emissions would bring about the same result.

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