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# AIR POLLUTION AND AIR QUALITY

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**A**ir pollution has been rising in most parts of the world for over a century. Among the reasons for this upward trend are rapid industrialization, the increasing concentration of population in urban areas, and a growing dependence on fossil fuels. Today, the amount of human-caused emissions released into the earth's atmosphere is a ubiquitous and complex problem. Evidence can be found everywhere—from city streets to lakes, streams, and soil, to the stratosphere. The consequences and costs are also mounting, whether measured in terms of deteriorating levels of human health, higher levels of acidity in water and soils, or by other standards.

Chapter 4 begins with a discussion of the monitoring system: its objectives, the location of monitoring stations, procedures for handling data, and related issues. Some of the most common parameters included in a program to monitor air quality are considered in the section Air Parameters. Brief descriptions of the methods of collecting and estimating data and the apparatus used are provided. Sources of emission and procedures for constructing emission inventories are considered in the

section Emission Sources and Inventories. The section Estimating Air Emissions describes the methods of estimating air emissions.

## Overview of a Monitoring Program

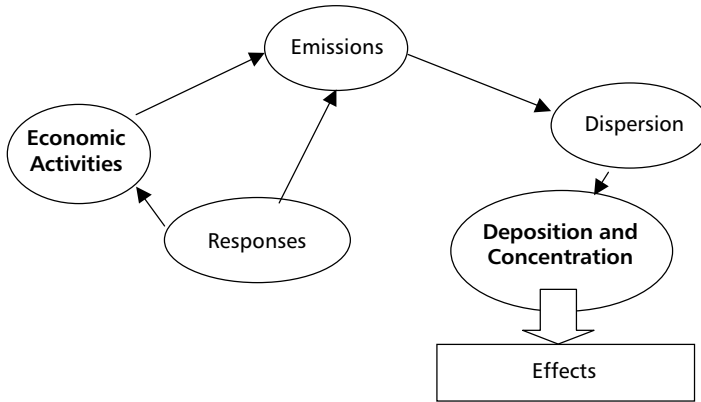
Figure 4.1 depicts the process of air pollution. Economic activities generate emissions (discharges from a source) which are then dispersed.<sup>11</sup> Wind is the main agent of dispersion. The physical character of the substances emitted may change or undergo a chemical reaction after release into the atmosphere. Substances can also adhere to suspended particulate matter (SPM). The process of deposition of an airborne pollutant can be either wet or dry. Substances that are dissolved or enclosed in water drops eventually fall to earth. In the case of dry deposition, substances are deposited on land or water through gravitation or are intercepted by some parts of the earth's surface such as mountains or forests.

Differences in a nation's priorities and environmental circumstances influence various aspects of a monitoring system. The availability of financial resources and human skills are other factors that are taken into account. Even industrialized countries find it necessary to limit their monitoring efforts. Decisions regarding the pollutants to be monitored, and the scope and quality of the data collected are all subject to these constraints.

**Monitoring objectives.** The design of any monitoring program—whether dealing with air, water, or other environmental media—starts with the identification of objectives. The explicit purpose is to collect data on specific parameters, but the ultimate objectives will be much broader. These goals need to be clearly defined to ensure that resources

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<sup>11</sup> Emissions can result from natural events as well as human activities. Examples of natural emissions include volcanic eruptions, forest fires, and radioactive decay. Pollution resulting from natural events can be substantial. This subject is included in the FDES, but is not discussed extensively here.

**Figure 4.1: Stages in the Process of Air Pollution**

are used efficiently and that acceptable results are obtained. Some examples of objectives that may be incorporated in any environmental program follow:

- (i) Assess the quality of the environment and enhance public awareness.
- (ii) Determine compliance with national or international standards.
- (iii) Assess population exposure and the impact on health.
- (iv) Identify threats to natural ecosystems and develop early-warning systems.
- (v) Identify sources of pollution and estimate pollutant loads.
- (vi) Evaluate the effectiveness of pollution control measures.
- (vii) Provide inputs for environmental management, traffic management, and land-use planning.

- (viii) Support the development of policies, the determination of environmental priorities, and other managerial decisions.
- (ix) Support the development and validation of managerial tools (for example, models and geographic information systems).

The choice of monitoring objectives will determine the degree of precision or quality of the data to be collected. Data of the highest quality is not always necessary, but it must be sufficient to satisfy the objectives. Statistical methods can be employed to help planners match issues of sampling frequency, data detail, and periodicity of monitoring with budget constraints.

Once the objectives have been fixed, a series of decisions need to be taken with regard to (i) the parameters to be monitored; (ii) the location and number of monitoring sites; (iii) sampling frequencies; (iv) the choice of monitoring equipment and sampling apparatus; (v) sampling methods and analytical techniques; and (vi) methods for data storage, retrieval, analysis, and interpretation.

***Air quality parameters.*** One of the most distinctive features of any program is the list of parameters to be monitored. Variations in national practices are great. Indeed, at the international level comparable data are available for just two parameters: SO<sub>2</sub> and SPM. As the number of motor vehicles has risen, more countries have begun to monitor traffic-related pollutants such as carbon monoxide (CO), nitrogen oxides (NO<sub>x</sub>), and lead (Pb). Ultimately, the selection of parameters must take into account the cost and complexity of gathering data for a specific pollutant and its relative significance for public health.

Whatever the initial combination of parameters, the list will certainly change over time. As the economy grows, the composition of human activities is altered and so, too, is the impact on the environment. New industries emerge and the fortunes of existing ones rise and fall. Additional investment brings new technologies while rising standards of living alter patterns of consumption. The interaction between these macroeconomic forces is too complex to describe here, but can be conveniently summarized by relating movements in an environmental parameter to changes in per capita income.

**Figure 4.2: Illustrated Effect of Changes in Per Capita Income on Environmental Parameters**

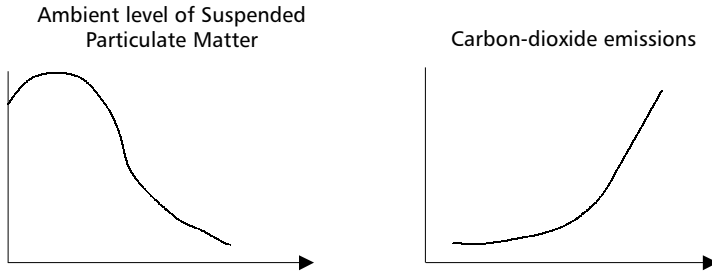


Figure 4.2 gives a stylized picture of this relationship for two parameters (SPM and  $\text{CO}_2$ ). The trends pictured are merely illustrations. They do not represent the experience of a specific country, but simply provide a rough indication of the changes that can be expected with economic progress. The ambient level of SPM tends to be especially high at low levels of per capita income. It may initially rise as per capita income begins to grow, but it falls off sharply as the country becomes richer. A quite different pattern is observed in the case of  $\text{CO}_2$ . At low levels of per capita income, the volume of emissions is modest because the country's fleet of cars and trucks is small. But the extent of car ownership rises quickly as per capita income increases, and the volume of emissions increases accordingly. The implication of such trends is clear. As growth and development continue, the list of parameters being monitored will have to be adjusted accordingly. The same applies to the mixture of environmental regulations and controls that are in place. Some may eventually become obsolete, while others must be introduced.<sup>12</sup>

<sup>12</sup> Environmental standards can also differ even among countries at the same stage of development. There are relevant differences in the way the receiving environment reacts to pollution. An oil spill in the stormy North Sea, for example, does less lasting damage than a spill off the almost tideless Mediterranean coast; contaminated land matters less when it is far from homes and reservoirs.

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**Monitoring stations.** A second crucial feature of the program is the network of stations used to collect data. Because air pollution is greatest in urban areas, the monitoring effort is usually concentrated in and around cities. Each geographic area has distinctive meteorological and topographic features and its own spatial distribution of air pollution sources.<sup>13</sup> The pattern of atmospheric dispersion is also unique for cities located in river valleys, coastal areas, or mountain valleys. Even within a particular city, pollution will vary with the terrain, elevation, meteorological conditions, traffic density, and time of day. Finally, seasonal variations must be taken into account. The concentration of air pollutants tends to be highest in the winter season when the least dilution and dispersion occur.

Improved quality is expected during the rainy season when most pollutants in the ambient air are washed to the ground by rainwater. The location of monitoring stations should take into account the ease of access to the site, the safety of the site, travel time to the laboratory (for quickly degrading samples), and the availability of power connections for monitoring equipment. Periodic visits to each site are also necessary to verify that no new emission sources that could jeopardize the representativeness of a site have appeared.

Clearly, a rather dense network of monitoring stations—coupled with frequent sampling from all locations—would be required to amass the raw data needed to construct representative indicators of air quality for an entire city or urban area. Such an elaborate network is rarely available, even in industrialized countries. At the other extreme, a minimum network of monitoring stations might consist of just a few monitoring stations in a residential zone, and a similar number located in an area with heavy motor traffic and in an industrial zone. Finally, additional data is needed to determine the baseline status, or background pollution, in the general area. This last set of monitoring stations should be located at sites representing all topographic features of the area, such as hilly terrain, valleys, and plains. The microclimatic conditions at each

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<sup>13</sup> The spatial pattern of pollution sources generally depends on factors such as the location of industrial enterprises that are heavy polluters, transport routes, and traffic patterns in the city.

of these locations will vary, influencing the dilution and dispersion of pollutants, and their ambient concentration.<sup>14</sup>

Most developing countries opt for something more than a minimum system, though not as elaborate as the versions found in industrialized countries. Some countries make use of intermittent or mobile sampling to reduce their resource requirements. These techniques, however, may not provide representative coverage with regard to temporal and spatial considerations. A more flexible approach is to set up monitoring stations or sampling points at carefully selected representative locations. Sites are chosen on the basis of the data required and any prior knowledge about emission and dispersion patterns of the pollutants being monitored. This approach generally requires fewer sites than other methods and, therefore, is cheaper to implement. In addition, various types of estimations may be needed to fill in the gaps in such a strategy.

Table 4.1 gives some examples of possible locations that may be part of this flexible approach. If previous compilations of emissions data are available, they will be helpful in choosing monitoring sites where population exposure is significant. Without such information, surrogate statistics—for example, population density, traffic flows, or fuel consumption—can be used to identify pollution hot spots. Should none of this information be available, special surveys may have to be designed to provide areawide or local information on pollution problems. These surveys often make use of either passive samplers or mobile monitoring laboratories, or both.

The frequency of sampling will depend on the range of variation in the parameters monitored, the concentration of pollutants, and the availability of financial and human resources. In the absence of any background data on parameters, an arbitrary frequency is chosen based on some knowledge of local conditions. Once sufficient data has been collected, the sampling frequency can be adjusted as required.

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<sup>14</sup> A methodology for handling large data sets and condensing the primary data into summary measures or indicators is provided in Appendix 3.

**Table 4.1: Possible Monitoring Sites Relevant to Exposure Assessment**

Site classification	Description
City/urban center	An urban location representative of general population exposure in the metropolitan center (e.g., pedestrian precincts and shopping areas)
Urban background	A site distanced from emission sources and therefore broadly representative of citywide background conditions
Suburban/residential	A location situated in a residential area on the outskirts of the city
Curbside/near road	A sampling site within 1-5 meters of a busy road
Industrial	An area where industrial sources make an important contribution to long-term or peak concentrations
Rural	An open countryside location distanced as far as possible from roads, and populated and industrial areas
Source/target-oriented	Any special, source-oriented site (for example, garages, car parks, or tunnels; or a site located at a targeted receptor point such as a school or hospital)

Source: Adapted from WHO (2000a).

**Monitoring technologies.** Monitoring operations can be carried out manually or with the help of automated equipment. The latter provides better reliability, more precise measurements, and the ability to monitor on a continuous basis. Automated equipment, however, is often expensive

and difficult to maintain. In contrast, manual methods are relatively inexpensive, easy to employ, and yield data of acceptable quality so long as methods allowing quality assurance and quality control are followed. Monitoring equipment is chosen after taking into account factors such as equipment costs and reliability and the desired quality of the data. Ultimately, the monitoring system may include a combination of automated and manual equipment. The types of equipment used include passive samplers, active samplers, automatic analyzers, and remote sensors. Their advantages, disadvantages, and approximate capital costs are given in Table 4.2.

When passive samplers are used, an "integrated air sample"—that is, a sample collected over a defined exposure time such as a week to a month—obtained by molecular diffusion to a pollutant-specific absorbent material. Pollutants collected in this way are analyzed in the laboratory. When active samplers are used, a known volume of air is pumped through a collector such as filter or an absorbent (typically a chemical solution) for a specified period of time. The pollutants captured are then sent for laboratory analysis. Finally, if automatic analyzers are employed, samples are collected and analyzed on-line and in real time, usually by electro-optical techniques such as ultraviolet or infrared absorption, fluorescence, or chemiluminescence. Monitoring methods that rely on remote sensors utilize long-path spectroscopic techniques to make real-time measurements of pollutants. Automatic analyzers and remote-sensing techniques do not require laboratory analysis.

**Quality assurance and quality control.** Whatever the degree of aggregation or complexity of the indicators being produced, statisticians must make every effort to ensure the credibility of their results. Procedures for quality assurance and quality control (QA/QC) are therefore an integral part of any monitoring program.

A program of quality assurance focuses on several premeasurement activities mentioned earlier in this chapter. A program of quality control, on the other hand, is concerned with measurement-related activities such as the calibration and operation of monitoring equipment (including laboratory equipment), data management, field audits, and the training of personnel involved in monitoring and laboratory analysis. Both

**Table 4.2: Assessment and Costs of Equipment for Air Monitoring**

Method	Advantages	Disadvantages	Capital Cost
Passive Samplers	Very low cost Very simple No dependence on electricity Can be deployed in large numbers Useful for screening, mapping, and baseline studies	Unproven for some pollutants In general provide only monthly and weekly averages Labor-intensive deployment/analysis Slow data throughput	US\$10-70 per sample
Active Samplers	Low cost Easy to operate Reliable operation/performance	Provide daily averages Labor-intensive collection and analysis Laboratory analysis required	US\$1,000-3,000 per unit
Automatic Analyzers	Proven High performance Provide hourly data On-line information	Complex and expensive to operate High skill requirements High recurrent costs	US\$10,000-15,000 per analyzer
Remote Sensors	Provide path or range-resolved data Useful near sources Multicomponent measurements	Very complex and expensive Difficult to support, operate, and calibrate Not really comparable with point data Subject to atmospheric visibility and interference	US\$70,000-150,000 per sensor, or higher

Source: WHO (2000b) .

components are essential to ensure successful implementation of any monitoring program. The purpose of QA/QC activities is to ensure that

- (i) measurements are accurate, precise, and credible;
- (ii) data are representative of ambient or exposure conditions;
- (iii) results are comparable and traceable;
- (iv) measurements are consistent over time;
- (v) data capture is extensive and evenly distributed; and
- (vi) resources are used in an optimal manner.

Table 4.3 lists the main components of QA/QC activities.

**Table 4.3: Major Components of Quality Assurance/Quality Control Activities**

Quality Assurance	Quality Control
Definition of monitoring and data quality objectives	Establish a chain for calibration/traceability
Network design, management and training systems	Network audits and inter-calibrations
Site selection and establishment	System maintenance and support
Equipment evaluation and selection	Data review and management
Routine site operations	

Source: WHO (2000).

**Data compilation and measurement.** The data collected via monitoring stations is often voluminous and is one of the major sources of information on air quality during the early stages of the program. Eventually, other data suppliers should emerge. Table 4.4 lists some potential contributors and the types of data they might provide. However, this network of data suppliers could take several years to develop and the following discussion focuses on the handling and use of information obtained through the monitoring system.

**Table 4.4: Potential Suppliers of Data on Air Quality**

Source	Type of data
Ministry of Environment/ Department of Environmental Protection	Ambient air quality data, data on emissions from various points sources
Ministry of Industry	Impact of industrial activities on air quality
Ministry of Housing	Air quality in residential areas, indoor air quality
Ministry of Agriculture	Air quality relating to agriculture and forests
Ministry of Transport	Air quality relating to traffic
Meteorological Institute	Rainfall, composition of rain, wind speed and direction, temperature, humidity, atmospheric pressure, etc.

At least two agencies have responsibilities relating to the data obtained from the monitoring system. Officials in the Ministry of Environment (or its equivalent) are usually in charge of the network of monitoring stations, the data bank containing all records of the monitoring

exercise, and several other functions.<sup>15</sup> Statisticians in the environmental statistics unit in the NSO have responsibility for a number of "downstream" operations such as the preparation of indicators and their subsequent dissemination. The methodologies employed to collect and store the monitoring results are primarily the responsibility of environmental authorities, but even at this stage the NSO has a role to play. Statisticians, for example, should be sure that their environmental counterparts follow internationally accepted methods for field and laboratory analyses and make use of international statistical classifications such as those developed by the UN and the Economic Commission for Europe (ECE).

Environmental authorities should also follow certain guidelines for compiling and validating of the information gathered by the monitoring system. The purpose of the guidelines is to facilitate subsequent tasks such as data standardization, transformation, and estimation.<sup>16</sup> The guidelines include the following:

- (i) Data recorded by each monitoring station should be stored separately, along with summary information on the air quality statistics at each monitoring site. These statistics should be readily available to all users.
- (ii) All air pollution concentration statistics should be accompanied by a description of the sampling and analytical methods used.

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<sup>15</sup> A useful distinction can be made between a database and a databank. The latter is a passive storage system where data are filed in the form delivered by the original supplier. In the database, data are selected according to defined criteria and transformed in accordance with a specific format to allow data handling and manipulation between files. A data bank would best describe the type of data collected from the monitoring system and stored by environmental officials. Once this data is transferred to the NSO, and possibly combined with data from other sources, it may be reformatted and undergo other statistical routines. At that point, the data collection would most accurately be described as a database.

<sup>16</sup> The guidelines are based mainly on ECE (1990) and ESCAP (1999).

- (iii) Any qualifying statements regarding the functioning of the monitoring station or the existence of unusual ambient conditions should be properly noted and stored along with the data collected.
- (iv) Any summary statistics on air quality for individual monitoring stations should be clearly linked to the specific geographical areas they relate to.

***Interpreting the results.*** Once data obtained through the monitoring process has been properly stored, the authorities will want to construct indicators that can be compared with national or international standards for long-term exposure to a pollutant. The options available depend on the number of monitoring stations, the frequency of samples taken, and the time period for which observations exist. With only a minimum amount of information, it is inadvisable for statisticians to produce aggregate indicators for an entire city or region. The differences between stations in terms of meteorological conditions and pollution patterns mean that such indicators have little reliability. In a minimum network, results are generally reported station-by-station. Essentially, the stations represent themselves. For each station, data can be reported as arithmetic means calculated for a specified period of time. Trend information can then be derived from the mean values and the results compared with the guidelines for acceptable long-term exposure to the pollutant.

Short-term exposure can be measured in percentile values (for example, the 95th or 98th percentile) to determine the occurrence of peak concentrations.<sup>17</sup> Alternatively, an observed high value—usually the second or third highest measurement in a sample—can serve this purpose. These indicators are used to assess the risk of short-term exposure by calculating the number of days per year (at a station) during which a guideline value or threshold for short-term exposure is exceeded.

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<sup>17</sup> An observation in the 95th percentile would mean that 95 percent of all observations fall below that value.

A more concise way of describing air quality would make use of average air pollution concentrations and changes in their values over time. Levels of concentration are typically expressed as mean values, calculated on the basis of daily or monthly values for each year. Supplementary information should also be produced describing the type of monitoring station, the surrounding land use or average traffic condition, the geographic location (elevation and terrain), dispersion characteristics based on local meteorology, methods used for air sampling and analysis, and major emission sources (motor vehicles, industrial establishments, and so on). The report for each station would also include the number of days per year the guidelines for pollutants are exceeded.

The types of indicators constructed on the basis of minimum data can highlight peak trends in pollutant concentrations at individual monitoring stations, but they cannot meet all of the needs of policy makers. Air (unlike water) is a continuous medium and statisticians will soon be under pressure to produce more general indicators for air quality. With only a very few monitoring stations, a brief historical series, and infrequent samples, this temptation should be resisted. However, as experience is gained and a more elaborate monitoring network is established, some generalizations can be considered.

Development of a more general set of indicators can be pursued on a step-by-step basis. Geographic integration is often the first phase. Statisticians can begin by identifying geographic areas that are homogeneous.<sup>18</sup> Monitoring facilities must be adequate throughout the designated area and meteorological conditions should be roughly comparable. Ultimately, this type of aggregation yields indicators for a single pollutant stated in terms of "urban peak concentration," rural peak levels," and so on, with the results compared with an appropriate national or international standard.

Figure 4.3 gives three examples of one approach, showing aggregates for concentrations of CO, SO<sub>2</sub>, and particulates as calculated by the

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<sup>18</sup> A rural-urban breakdown is the most common division into homogeneous areas. However, even some rural areas may include one or more establishments that are significant polluters. A careful assessment is therefore essential.

Department of Environment, Transport and the Regions in the United Kingdom. The results are presented as simple line graphs stated in terms of the composite average and range (maximum and minimum). Such figures can be readily interpreted by the public and nonexpert decision makers to identify trends, compare levels with national or international standards, and assess progress toward long-term objectives.

Prior to the preparation of these aggregates, the underlying data was subjected to an elaborate series of tests to ensure that only reliable, quality-controlled data was used. The purpose of the tests was to determine whether there was a good reason to exclude data from certain monitoring sites. The main reasons for ultimately excluding data follow:

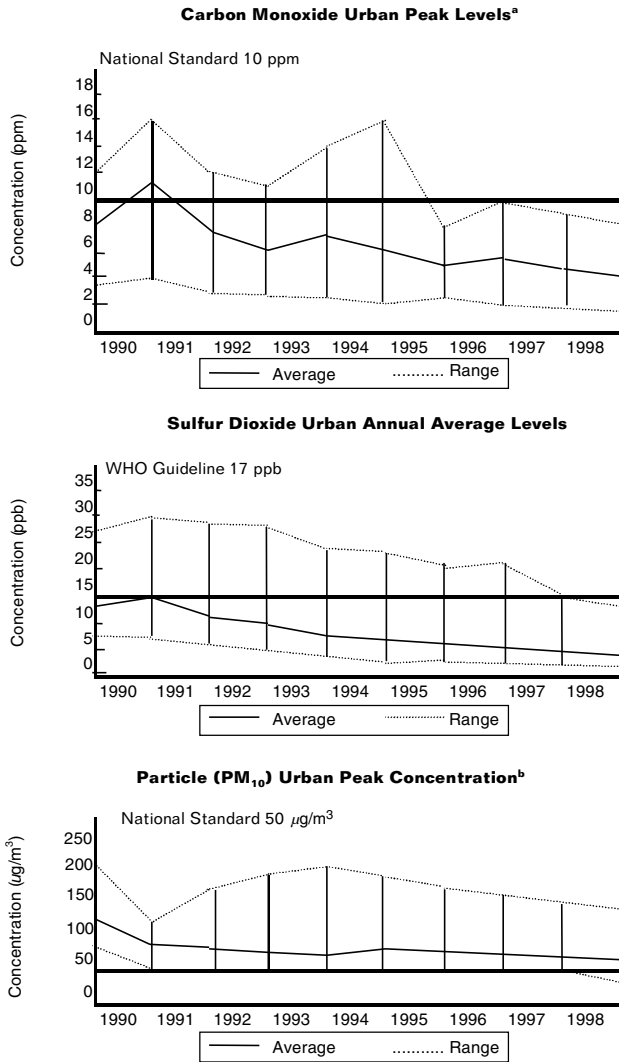
- (i) inadequate data capture in a specific year;
- (ii) a discontinuous data record, usually because a monitoring site was unable to contribute data to the aggregate indicator in every year;
- (iii) trends that were not representative, typically because the data collected at a site was inconsistent with data observed at other sites.

At a later stage in the development of the program, statisticians may choose to go beyond the geographic integration of indicators for individual pollutants so as to produce a single air pollution or "headline" indicator. This indicator will have to be based on the combined measured concentrations of different pollutants. A composite indicator of this type cannot be developed without abundant and ratified data, and numerous tests to demonstrate the robustness and representativeness of the measure.<sup>19</sup>

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<sup>19</sup> For a discussion of this process and a description of the tests applied, see ECE (1999), pages 6-9.

**Figure 4.3: Reported Indicators of Air Pollution in the United Kingdom**



<sup>a</sup> Peak measurements for carbon dioxide are running 8-hour means in a year.

<sup>b</sup> Peak measurements of particulates (PM<sub>10</sub>) are represented by the 99th percentile of daily maximum running 24-hour means.

Source: ECE (1999).

In conclusion, the statistics gathered by the monitoring system pass through several stages as environmental specialists and statisticians work to transform the raw data into information that can be used by health authorities, regulatory officials, and the general public. An overview of the complete process is presented in Figure 4.4. A minimum level of data production can include provision of daily, monthly, and annual summaries with simple statistical and graphical analyses that show both time and frequency distributions of the monitoring data. The information and indicators derived from these sources must be reported or disseminated in a timely fashion to end users.

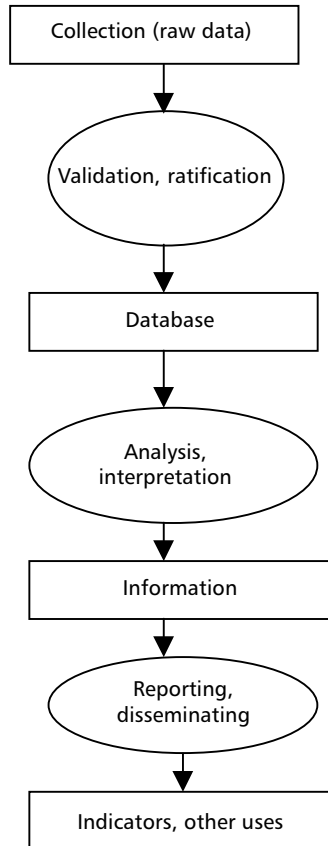
## Air Parameters

The air pollutants monitored in most countries generally fall into three broad categories: gaseous pollutants, SPM, and odors. Some of the common gaseous pollutants are ammonia,  $\text{SO}_x$ ,  $\text{NO}_x$ , CO, and hydrocarbons. These gases, along with SPM, are generated by both stationary and mobile sources.<sup>20</sup> Hydrogen sulfide and mercaptans are two ubiquitous odorous gases and their emissions are usually attributed to industrial sources or to natural geothermal sources. All these air pollutants are harmful to human health. Any comprehensive program of air pollution management should monitor their presence regularly. An overview of the monitoring techniques, sampling methods, and equipment requirements for each of the eight pollutants noted above is given in this section. Meteorological parameters such as temperature and humidity are also considered.

***Meteorological parameters.*** A number of meteorological parameters can influence the patterns of dilution and dispersion of atmospheric pollutants. The most important of these parameters are

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<sup>20</sup> The most important stationary sources of emissions are industrial establishments; certain process emissions occurring in agriculture, mining, and quarrying; and emissions by households such as from heating and cooking. Various categories of emissions are discussed in the section on Emission Sources and Inventories.

**Figure 4.4: Stages in Processing Data in a Monitoring System**

temperature and its changes with altitude, the mixing height (that is, the height above ground where the pollutants diffuse), wind speed and direction, atmospheric pressure, and humidity. Any comprehensive program to monitor air quality will need to take these factors into account.

**Temperature.** In a regular monitoring program several measurements of temperature will be required, including the daily mean temperature, and daily maximum and minimum. Different types of thermometers are used for these purposes. The basis for measuring the temperature of an object is any physical property of the object that is a

function of temperature. Alterations in the physical property of the object must be proportional to alterations in temperature recorded by the thermometer. When measuring atmospheric temperature, the physical properties most widely used are thermal expansion and changes in electrical resistance. Depending on the physical property chosen, the most common thermometers used for this purpose are a liquid-in-glass type or an electrical type.

Certain safeguards must be taken to ensure the accuracy of measurements. Specifically, if a thermometer is in the air and directly exposed to solar radiation, some of this radiation can be absorbed. The instrument may then give a reading higher than the actual air temperature. To protect the thermometer from direct exposure to solar radiation, it is installed under a screen or shield. The screen or shield also protects the thermometer from precipitation and prevents accidental damage. There should be ample space between the instrument and the walls of the screen to ensure that there is no physical contact. Most screens allow natural ventilation or free circulation of the air surrounding the thermometer. The walls of the screen are usually double-louvered, and the roof is double-layered, with provisions for ventilation of the space between the two layers. Free circulation of air through the screen allows the temperature of the inner wall to adapt to ambient changes. The floor of the screen should be designed for easy removal of snow and ice in cold climates. Normally, the screen with the thermometer inside is mounted at a height of 1.25-2 meters above the ground when measuring free air temperature over a large area.

Air temperatures-including the daily mean, minimum, and maximum-are routinely monitored using a liquid-in-glass thermometer. This thermometer relies upon the differential expansion of a pure liquid with respect to its glass container to indicate temperature changes. Mercury is commonly used as the liquid to measure the temperature in higher ranges, while ethyl alcohol or another pure organic liquid is used for lower temperature ranges. A liquid-in-glass thermometer has two components: a bulb where the liquid is stored, and a stem or tube with a fine bore attached to the main bulb. The bulb is completely filled with the liquid, while the stem is partially filled at all temperatures. As the

temperature rises, the liquid in the bulb expands and moves up to the stem. Changes in temperature are indicated by changes in the length of the liquid in the stem, which is calibrated with respect to a standard thermometer. A scale of temperature is marked on the stem, or on a separate scale tightly attached to the stem to record readings.

Maximum temperature is measured by a mercury-in-glass thermometer with a constriction in the bore between the bulb and the beginning of the scale. The constriction prevents the mercury column from falling when the temperature drops. The thermometer is mounted at an angle of about two degrees from the horizontal with the bulb at the lower end to ensure that the mercury column in the stem rests against the constriction and does not fall by the force of gravity. When measuring minimum temperatures, a thermometer containing spirits, ethyl alcohol, pentane, or toluol is used. The thermometer has a dark glass index immersed in the liquid. Like the maximum-temperature thermometer, the minimum-temperature model is mounted at a near horizontal position.

Thermometer readings should be taken carefully and precisely to avoid any alteration of temperature due to the direct exposure of the sensor to sunshine or snow when the screen door is opened. Observers must also take care to avoid parallax error (an error made by the observer while taking readings due to the wrong positioning of the eye and the thermometer scale). Readings from both the maximum and minimum thermometers should be taken and reset at least twice daily. The readings should also be compared regularly with measurements from a standard thermometer to ensure that there are no errors.

Manual means of recording temperatures from the thermometers through direct observation do not give continuous results. Mechanical thermographs make use of bimetallic or Bourdon-tube sensors for continuous recording in a graph. Thermographs are prepared by a rotating chart mechanism. These devices are relatively inexpensive, easy to operate, reliable, and portable. Bimetallic thermographs rely on the movement of a recording pen, which is controlled by temperature-induced changes in the curvature of a bimetallic strip or helix, one end of which is rigidly fixed to an arm attached to the frame of the instrument. While the general mechanism of a Bourdon-tube thermograph is similar to that of a

bimetallic thermograph, its temperature-sensitive element is in the form of a curved metal tube with a flat elliptical section, filled with alcohol.

Electrical thermometers are generally used for automatic and continuous measurements of temperature. These thermometers produce an output signal proportionate to the change in temperature. They are suitable for use in remote locations, and for recording, storing, and transmitting data to the monitoring station. The most common types of electrical thermometers are electrical resistance elements, thermistors, and thermocouples. More advanced devices employ digital measuring techniques and are used when the output data for a large number of monitoring stations are recorded and processed in a digital computer. The accuracy and precision of the digital technology are high.

**Humidity.** When measuring humidity, analysts can choose from four basic methods:

- (i) thermodynamic methods (psychrometers),
- (ii) methods based on the change in dimensions of hygroscopic substances (hair hygrometers),
- (iii) methods relying on the change of electrical resistance due to absorption or adsorption, and
- (iv) condensation method (dew- or frost-point hygrometers).

Techniques relying on condensation and electrical resistance are used in automatic meteorological monitoring stations and are frequently employed for upper-air measurements.

Two types of psychrometers are available: a stationary screen version and the portable Assman or whirling version. In the typical meteorological station, stationary screen psychrometers are used to measure humidity in the air. The device consists of two mercury-in-glass thermometers and dry-bulb and wet-bulb thermometers, which are installed under a screen to protect them from direct radiation. The metallic shields are separated from the rest of the apparatus by insulating materials.

Adequate space and ventilation are provided for free movement of the air surrounding the thermometers. The dry-bulb thermometer is a normal thermometer similar to that used for recording normal air temperature. The wet-bulb thermometer contains liquid mercury that is moistened by wet muslin dipped into distilled water and kept in a wick. Water from the wet-bulb thermometer evaporates and lowers its temperature reading, while the dry-bulb thermometer shows the corresponding air temperature at any given point of time. The difference in the readings of the two thermometers is recorded. Atmospheric humidity is calculated from a standard chart that indicates the empirical relationship between the difference in temperature readings of the dry- and wet-bulb thermometers and the relative humidity in air.

Care should be taken to ensure that thermometers are not exposed to direct sunshine or frost when readings are being taken. The muslin cloth and the wick in the wet thermometer should also be cleaned regularly to prevent contamination. For continuous monitoring of atmospheric humidity, thermographs are prepared from the readings of the dry- and wet-bulb thermometers.

The hair hygrometer is useful for measuring atmospheric humidity in conditions where extreme temperatures and very low humidity are rare. Electrical thermometers are increasingly used to record dry- and wet-bulb temperatures because they give more precise and accurate results. Dew-point hygrometers are used as a reference standard for determining dew point or frost point in the atmosphere. They are very expensive devices.

**Rainfall.** Measurements of rainfall should be designed to capture a sample representative of the true amount falling over the area to be monitored. Measurements can be conducted either with manual, nonrecording instruments or with continuous recording devices. Nonrecording rain gauges are the most widely used method for measuring rainfall. These are open receptacles with an orifice where rainfall is collected. The amount collected in a gauge is measured with a graduated stick to determine the depth. Alternatively, rainfall can be determined by measuring the volume or weighing the contents. The volume of the gauge and its orifices should be adjusted for the expected rainfall of the area. Normally, gauges are placed at ground level with

the base firmly mounted to withstand the force of strong wind and to avoid toppling.

Rain gauges are preferably kept at a site free from any physical obstacles. If that is not possible, the site should be so chosen that no object is closer to the gauge than a distance twice the obstacle's height above the gauge orifice. To avoid rainwater splashing into the gauge, the gauge should not be located on a hard, flat or concrete surface.

Two types of nonrecording rain gauges—standard and storage gauges—are available. Standard gauges are used to record daily, weekly, or monthly measurements. They normally consist of a collector placed above a funnel leading into a container. The collector has a vertical wall deep enough to prevent rain from splashing in and out, and the slope of the funnel must be sufficiently deep (at least  $45^\circ$ ). The container should have a narrow entrance to minimize the loss of collected rainwater through evaporation due to solar radiation. Rain gauges used to measure weekly or monthly rainfall should have a larger capacity and stronger construction.

Storage gauges are used to measure total seasonal rainfall in remote areas. The components are similar to those of standard gauges, but the container is large enough to store the seasonal rainfall. An antifreeze solution such as ethylene glycol or a mixture of ethylene glycol and methanol can be kept in the container to convert any snow falling into the gauge into a liquid state and to prevent rainwater from being converted into snow in cold weather. A layer or thin film (0.5 mm) of evaporation suppressant should be placed in the container to reduce evaporation. When an ordinary, nonrecording rain gauge is used, measurements are taken with the help of a graduated measuring cylinder made of glass or plastic. Another alternative is to use a graduated dip rod of cedar wood or some other material that does not absorb water appreciably and possesses only a small capillary effect.

Three types of recording gauges are available to measure rainfall. These are the weighing type, a tilting or tipping-bucket type, and a float gauge. If the weighing-type instrument is used, the container, together with the rainfall in it, is weighed continuously by means of a spring mechanism or a system of balance weight. The float-type instrument allows rain to pass into a chamber containing a light float. The rainfall

passes into the float chamber, causing the float to rise. The vertical movement of the float is transmitted through a suitable mechanism to the proportional movement of a pen on a chart, recording rainfall on a continuous basis.

When a tilting-bucket gauge is used, rainfall is collected in one of two chambered buckets that are balanced in unstable equilibrium about a horizontal axis. In its normal position, the bucket rests against one of its two stops. Rainwater flows from a collector into the uppermost compartment of the bucket. After a predetermined amount of rainwater enters the compartment, the bucket becomes unstable and tips over to a rest position, with the other compartment now placed in a position to collect rainwater. The shape of the bucket compartments is such that rainwater is emptied from the lower one. The time when each bucket tips over and spills a specified quantity of water is recorded and the total amount of rainfall can then be determined.

Continuous recording of rainfall can be obtained with the use of any of these devices by preparing a chart, or by mechanically or electronically converting the values to a digital form that is recorded at uniform time intervals. The movement of a float, bucket, or weighing can also be converted into an electrical signal that is received at a distant monitoring station.

**Sulfur dioxide.** This gas is one of the major pollutants generated during the combustion of fossil fuels (for example, power generation and automobile exhaust) and other industrial activities such as smelting of sulfur-containing ores, manufacture of sulfuric acid, and petroleum refining.  $\text{SO}_2$  is partially oxidized in the air to form sulfur trioxide, a compound that readily combines with water vapor to form sulfuric acid. When sulfuric acid is present in the atmosphere, it contributes to acid rain.

Like SPM,  $\text{SO}_2$  can be monitored manually or with automated equipment. Manual techniques may be static or mechanical, but the latter is preferred due to its proven reliability and relatively moderate capital and operating costs. When mechanical techniques are employed, a measured volume of air is sucked into the monitor with the help of an air pump (blower). The air is drawn in at a specific flow rate (for example, 0.5 liter/minute or 1 liter/minute) for a specific period of time (1 hour, 4

hours, or 24 hours). The air stream passes through a prearranged number of bubbler/impinger tubes. These tubes have inlet and outlet devices to allow the air to pass through. They are filled with a reagent that absorbs the SO<sub>2</sub> present in the air to form a complex. This complex is then made to react with other chemicals to form a second, colored complex. The intensity of the color is measured by means of a colorimeter or spectrophotometer, and can be directly related to the amount of SO<sub>2</sub> present in the corresponding air sample by means of a calibration curve.

The sampling period with manual techniques varies from 30 minutes to 24 hours, depending on the expected pollution levels. Short-term sampling conducted during a period ranging from 30 minutes to one hour is common practice when high levels of SO<sub>2</sub> concentration are expected. Long-term sampling over a 24-hour period is done when relatively low concentrations are anticipated.<sup>21</sup> Different combinations of absorbing reagent volumes, sampling rates, and sampling times can be chosen, depending on the specific requirements. Sample volumes must be adjusted so that linearity between the absorbance and concentrations is maintained. In most instances, sampling is carried out at least twice a week at any monitoring station.

The apparatus required for manual monitoring with mechanical equipment include a bubbler/impinger tube, an air pump/blower, a flow-control device, a membrane or glass fiber filter, flow calibration equipment, a timer, a spectrophotometer, and a thermometer.

The concentration of SO<sub>2</sub> can be determined according to the following equation:

$$\text{SO}_2 (\mu\text{g}/\text{m}^3) = \frac{(A - A_0) \times 10^3 \times B_g}{V_r} \times D$$

<sup>21</sup> A high level of concentration would be one close to or exceeding 1,000 μg/m<sup>3</sup>. A low level of concentration would be 25 μg/m<sup>3</sup> or less.

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Where	A	=	sample absorbance
	$A_0$	=	reagent blank absorbance
	$10^3$	=	conversion of liters to cubic meters
	Vr	=	the sample volume corrected to 25°C and 760 mm Hg, liters
	$B_g$	=	the calibration factor, mg/unit of absorbance
	D	=	dilution factor

Automated techniques for continuous  $\text{SO}_2$  monitoring are employed in air pollution control programs that mandate a continuous record. The availability of automated equipment simplifies several of the analytical steps that must be performed manually when mechanical equipment is used. Automated techniques, however, are expensive.

Automated monitoring can be based on any of several sophisticated principles relating to conductivity, colorimetry, electrochemical diffusion, gas chromatography coupled to flame photometry, and ultraviolet fluorescence (UVF). The most popular and widely used method is the UVF technique. With this method,  $\text{SO}_2$  molecules in the sample air stream are excited to an unstable energy state by ultraviolet radiation. This high energy state decays with emission of secondary fluorescence radiation. The intensity of the fluorescent radiation is proportional to the concentration of  $\text{SO}_2$  present in the air sample. The apparatus required for continuous monitoring varies, depending on the type of analytical technique chosen.

**Oxides of nitrogen.** These gases are the products of high-temperature combustion of fossil fuels. They are created during various industrial processes such as power generation, the use of industrial boilers and diesel generators, petroleum refining, and the production of inorganic chemicals (for example, nitrogenous fertilizers). The automobile exhaust from diesel-run vehicles is another important source. The most common gases of this type are nitric oxide and nitrogen dioxide.<sup>22</sup> Like  $\text{SO}_2$ ,  $\text{NO}_x$  contribute to the formation of acid rain.

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<sup>22</sup> Nitrous oxide is also formed in the atmosphere. In that case, however, it results mainly from biological activity in the soil and is not considered to be a pollutant.

Monitoring operations are conducted with either passive or active samplers. A process of passive sampling makes use of diffusion tubes to determine the average concentration of  $\text{NO}_x$  during the exposure period, which typically ranges between two and four weeks. This method is particularly well suited for baseline studies and for assessing the spatial distribution of  $\text{NO}_x$  in an urban environment. A passive tube sampler uses a chemical as an absorbent to determine the amount of  $\text{NO}_x$  in the atmosphere. After thermal desorption, the sample is analyzed by spectrophotometry or by ion exchange chromatography. This method is widely used in the United Kingdom and Europe.

Manual or automated means can be used for active sampling of  $\text{NO}_x$ . Manual sampling is a semicontinuous method. In this case, a measured volume of air is sucked into the sampler with the help of an air pump (blower). The air enters at a specified flow rate (0.3 liter/minute to 0.6 liter/minute) during a specific period. The air stream passes through a prearranged number of bubbler/impinger tubes (glass tubes with inlet and outlet devices). The tubes are filled with a reagent, which absorbs the  $\text{NO}_x$  in the sample air and forms a complex. This complex, in turn, is made to react with other chemicals to form another highly colored complex (an azo-dye). The intensity of the color of the complex is measured by means of a colorimeter or spectrophotometer, and can be directly related to the amount of  $\text{NO}_x$  present in the air sample by means of a calibration curve. The manual method is relatively simple to implement and the apparatus required is inexpensive.

The sampling period for the manual technique may vary from 15 to 30 minutes for short-term sampling and from 4 to 24 hours for long-term sampling. The choice of a sampling period depends on the expected pollution levels—that is, the concentration of  $\text{NO}_x$  in the ambient air at the monitoring station and the monitoring procedure used. The volume of absorbing reagents used, the volume of the sample collection, and sampling rate are adjusted to match the duration of the sampling period. Sampling should be carried out at least twice a week at each monitoring station.

The monitoring equipment includes a bubbler/impinger tube, an air pump/blower, a flow control device, a membrane or glass fiber filter,

flow calibration equipment, a timer, a spectrophotometer, and a thermometer.

Estimates of the concentration of  $\text{NO}_x$  in the ambient air are based on the following equation:

$$\text{NO}_x \text{ } (\mu\text{g}/\text{m}^3) = \frac{(A - A_0) \times Y}{V} \times D$$

Where	A	=	sample absorbance
	$A_0$	=	reagent blank absorbance
	Y	=	volume of absorbing reagent, ml
	V	=	the sample volume corrected to 25°C and 760 mm Hg, $\text{m}^3$
	D	=	constant

Automated techniques for continuous monitoring of  $\text{NO}_x$  are used in pollution control programs that mandate continuous records and for checking regulatory compliance. Several types of automated analyzers are available. They make use of various techniques such as colorimetry, NDIR, and chemiluminescence. All automatic devices monitor nitric oxide (NO) and nitrogen dioxide ( $\text{NO}_2$ ) separately. The results are then summed to determine the total concentration of  $\text{NO}_x$  in the ambient air. Alternately, one oxide can be converted into the other before the measurement is made.

Among the various automated devices available, the chemiluminescence technique is the most popular because it is relatively cheap, and accurate, and is applicable to a wide concentration range. When using this method, NO is made to react with ozone to form  $\text{NO}_2$  and oxygen. Part of the  $\text{NO}_2$  (about 7 percent) remains in an excited state, which then reverts to the ground state with emissions of radiant energy. The emitted radiation is received by a photomultiplier tube, whose output is amplified and fed to a recorder. The intensity of this radiation is proportional to the amount of NO present in the sample air.

After its conversion to NO, concentrations of  $\text{NO}_2$  in the ambient air can also be measured by this device. Air samples are directly drawn

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into the analyzer to establish an output signal for NO. A switching valve then directs the air sample through the converter where NO<sub>2</sub> is converted quantitatively to NO. The detector then records a signal for total NO<sub>x</sub>. Finally, the concentration of NO<sub>2</sub> is measured by subtracting, electronically, the NO signal from the signal for total NO<sub>x</sub>. The time required to monitor NO<sub>x</sub> in a chemiluminescence device is generally less than a minute. The apparatus required for this technique includes a particulate filter, a thermal converter, an ozone generator, a reaction chamber, and a vacuum pump.

***Suspended particulate matter.*** Airborne particulates, known as SPM, come in many sizes. The larger, coarser types of particles are a local nuisance, contributing to poor visibility and soiling. However, smaller particles have serious consequences for the health of those exposed to them because they can penetrate deep into the lungs and airways. Most the SPM released into the air comes from industrial processes that involve the handling of materials (including loading and unloading) and the combustion of fossil fuels. Automobile exhaust is another major source of particulate matter.

SPM can be monitored using either manual or automated equipment. Manual techniques may be static or mechanical, but the latter is generally preferred due to its proven reliability and modest capital and operating costs. In the manual process, SPM is measured gravimetrically using electrically powered samplers. The samplers are equipped with an air pump/blower that draws in ambient air at a constant volumetric flow rate for a specific period of time. The air to be sampled passes through a glass fiber filter of known weight. The weight of particulate matter deposited on the filter can be used to calculate the mass concentration of SPM in the ambient air when the mass of collected particulate is divided by the volume of air sampled. This method is applicable for measuring the mass concentration of all particulate matter with a diameter ranging between 0.1 and 100 micrometers.

The sampling period can vary, depending on the concentration of SPM in the ambient air. If the ambient concentration is expected to be low, each sample is collected continuously over a 24-hour period. When the level of SPM is expected to be high, a sampling duration of 6-8 hours is adequate for each sample.

The gravimetric technique can also be used to determine the concentration of finer particles in the ambient air. When measuring the ambient concentration of particles of 10 micrometers ( $PM_{10}$ ) or less, the air sampler draws ambient air at a constant flow rate into a specially shaped inlet where the particulate is inertially segregated into one or more size fractions within the  $PM_{10}$  size range. Each size fraction of particulate is then collected on a separate filter paper for a specified sampling period.

When particulate matter in a size range of 2.5 microns ( $PM_{2.5}$ ) is to be tested, ambient air is drawn into a specially shaped inlet at a constant volumetric flow rate for a specific period of time. As the air is drawn in, it passes through an inertial particle size separator or impactor. Typically, the designed flow rate for  $PM_{2.5}$  through the inlet is 1,000  $m^3$ /hour measured as actual volumetric flow rate at the temperature and pressure of the sample air entering the inlet. Particles in the size range of  $PM_{2.5}$  are separated from the sample air for collection on a polytetrafluoroethylene filter.

The apparatus used in these operations include a sampler (with air pump/blower), a sampler shelter, a flow recorder and flow controller, an orifice calibration unit, a timer, membrane or glass fiber filter, a manometer, a barometer, a thermometer, and an analytical balance.

The calculation for these tests makes use of the following equation:

$$SPM (\mu g/m^3) = \frac{(W_f - W_i)}{V_T} \times 10^6$$

Where  $W_f$  = final weight of filter, grams  
 $W_i$  = initial weight of filter, grams  
 $V_T$  = total volume of air sampled, cubic meters  
 $10^6$  = conversion of gram to microgram

Automated techniques for continuous monitoring of SPM are usually employed in air pollution control programs that mandate continuous record. They may also be used for checking regulatory compliance. These techniques are comparatively expensive and specialized

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skills are required to handle the equipment. Three choices of automatic techniques are available:

- (i) tapered element oscillating microbalance (TEOM),
- (ii) beta-ray absorption analyzers, and
- (iii) light scattering systems.

Of the three, the TEOM and beta-ray systems are widely used and thoroughly tested. The light-scattering device was developed recently and is less proven.

**Carbon monoxide.** One of the most common and widely distributed gaseous pollutants, CO results primarily from the incomplete combustion of carbonaceous materials. The principal sources are automobile exhaust, space heating, municipal and industrial incineration, and burning of wastes. Other sources include power plants, industrial boilers, diesel generators, coke ovens, blast furnaces, steel furnaces, organic chemicals, and petroleum refining.

CO is a colorless, odorless, tasteless, and stable gas that is lighter than air. In high concentrations, it causes various physiological changes and, eventually, death. Regular exposure at low concentrations can also have a significant impact on health. Industrial workers and urban inhabitants who are repeatedly exposed to this gas suffer from various illnesses.

A variety of techniques can be used to monitor the amount of CO in the ambient air. They include a continuous method known as NDIR technique, a gas chromatographic technique (semicontinuous method), an electrochemical technique (continuous method), an infrared spectrophotometric method, a semiquantitative detector tube technique, and a colorimetric method. Of these, the most common is the NDIR spectrophotometric technique. This is an automated method, which is generally regarded as the most reliable alternative. The NDIR technique depends on the absorption of infrared radiation by CO. The analyzers on which the technique is based have several advantages, being relatively

insensitive to flow rates, reasonably independent of changes in the temperature of the ambient air, and offering a short response time. A drawback is that this method (like others) is insensitive to low-level concentrations of CO.

The analyzer used in the NDIR spectrophotometric technique consists of a sample cell, a reference cell, two infrared sources, and a detector cell. The reference cell is filled with a nonabsorbing gas such as nitrogen, and the sample cell is continuously flushed with the sample (ambient air). The CO in the air absorbs radiation emitted from the infrared source at wavelengths between 4.5 and 4.9 micrometers. The detector is made up of two compartments separated by a thin metal diaphragm and filled with CO.

If there is no absorbing gas in the reference cell, most of the infrared energy emitted from the source is transmitted to one compartment of the detector cell. The remainder of the infrared energy—an amount inversely proportional to the concentration of CO in the sample—reaches the other compartment of the detector cell. The unequal amounts of infrared radiation transmitted to the reference cell and the sample cell result in a pressure difference across the diaphragm which, in turn, causes the diaphragm to pulse back and forth. Displacement of the diaphragm is detected electronically and amplified to produce an output signal that is recorded. The signal provides a measure of ambient carbon CO. The NDIR method can also be used for the analysis of batch-type samples collected in bags or evacuated cylinders from the ambient air. Commercial NDIR analyzers can detect CO concentrations ranging between 0 and 100 parts per million (ppm).

**Hydrocarbons.** Hydrocarbons are a group of gaseous pollutants generated by automobile exhaust and industrial processes such as petroleum refining, and roasting and heating processes in ferrous metallurgical units and organic chemical units. Both methane and nonmethane hydrocarbons are found in the air. The methane version is more abundant and generally less hazardous than nonmethane hydrocarbons. Hydrocarbons themselves, are not particularly harmful when released into the air. However, in the presence of sunlight they undergo chemical reactions with NO that are also present in the

atmosphere to form "photochemical oxidants." These oxidants pose a real threat to human health and agriculture. Nonmethane hydrocarbons, which have a higher level of photochemical activity than methane hydrocarbons, are a more serious problem.

The analysis of hydrocarbons in the atmosphere consists of a three-step procedure involving collection, separation, and quantification. In the first step, the sample air is drawn with the help of a pump. The air enters an evacuated canister (cylindrical tube) at a specific, predetermined rate for a specific period of time. Air containing methane and nonmethane hydrocarbons is then passed through a gas-chromatography column, where the two classes are separated. Separation is based on the different adsorption/desorption rates of the absorbent materials present in the column. When the methane and nonmethane hydrocarbons exit the column, they are injected into a device known as a flame ionization detector (FID). In the FID, the sample gas is injected into a flame created by burning hydrogen in either air or oxygen. As the two classes of hydrocarbons are burned, they release ions creating electrical currents across the electrodes inside the FID. These currents are amplified and displayed on an output meter/detector. The signal output of the detector is proportional to the two groups of hydrocarbons and is quantified when compared with standard concentrations of hydrocarbon free gases. Results of the monitoring can be expressed in parts per million by volume (ppmV) or parts per million by carbon (ppmC).

**Hydrogen sulfide.** This is an odorous gaseous pollutant that is offensive at low concentration and toxic at high concentrations. Repeated exposure to low concentrations of hydrogen sulfide ( $H_2S$ ) has an irritating effect on the mucus membranes, eyes, and the respiratory tract.  $H_2S$  is generated from geothermal sources, anaerobic biodegradation (in the absence of oxygen) of municipal garbage at landfill sites, and industrial processes such as roasting and heating processes in ferrous metallurgical industries, and the krafting process in the pulp and paper industries.

$H_2S$  can be monitored manually or with automated equipment. The manual technique is similar to that used for  $SO_2$  and  $NO_x$ . A measured volume of air is drawn at a specific flow rate (1.5 liters per minute) for a specific period of time (up to two hours) with the help of a blower and

passed through impinger tubes containing a reagent that reacts with the  $H_2S$  to form a complex. This complex is then made to react with other reagents to form a colored complex, the intensity of which is measured with the help of a spectrophotometer or colorimeter. The concentration of  $H_2S$  can be calculated from the spectrophotometer or colorimeter reading with the help of an empirical relationship based on the recorded absorbance and the concentration of  $H_2S$ .

The equipment required for this operation includes an impinger tube, an air pump/blower, a flow control device, flow calibration equipment, a timer, spectrophotometer/colorimeter, and a thermometer. The amount of  $H_2S$  present in a sample can be determined using the following equation:

$$H_2S (\mu g/m^3) = \frac{(A - A_0) \times 10^3 \times B_g \times V}{V_s A}$$

Where	A	=	sample absorbance
	$A_0$	=	reagent blank absorbance
	$10^3$	=	conversion of liters to cubic meters
	$B_g$	=	calibration factor, mg/unit of absorbance
	V	=	volume of absorbing solution, ml
	$V_s$	=	volume of sample air corrected to 25°C and 760 mm Hg, liters
	A	=	volume of aliquot, ml

Increasingly, the atmospheric concentration of  $H_2S$  is being monitored by automatic, continuous methods. In this case, the ambient concentration is determined by measuring the change in reflectance due to the formation of a complex from the reaction between  $H_2S$  and a reagent. The sample air is passed through a flow meter and a humidifier that maintains constant humidity in the reaction chamber required for the reaction, and then on a reagent (lead acetate) impregnated on paper tape.  $H_2S$  in the sample air reacts with the reagent on the tape (known as a sensing tape) to form a complex of lead sulfide. This reaction alters the reflectance of the sensor/paper tape due to the darkening caused by the

complex. The resultant change in reflectance is detected by a photocell. Output from the photocell is transferred to an electronic device that produces a proportional signal, which is amplified and recorded continuously on a chart. A chart speed of 1 cm/minute is suitable for short-term analysis, and a chart speed of 1-5 cm/hour for long-term sampling. The rate of change in reflectance is proportional to the concentration of H<sub>2</sub>S in the sample air.

The equipment used for monitoring includes a H<sub>2</sub>S analyzer, which consists of a flow meter, a humidifier, a sensing surface exposure chamber, an optical system/photo cell, and an electronic detector, bubbler, pump, and recorder.

The concentration of H<sub>2</sub>S is calculated using the following equation:

$$\text{H}_2\text{S (ppb/v)} = c(\mu - b)/(r - b)$$

Where c = concentration of reference standard, ppb/v  
 $\mu$  = unknown sample analyzer reading,  
 as received percent of scale  
 b = blank analyzer, percent of scale  
 r = reference standard analyzer reading,  
 percent of scale

***Mercaptans.*** These are odorous, gaseous compounds that are offensive at low concentrations and toxic at higher concentrations. Mercaptans are produced from geothermal sources, industrial processes (for example, the krafting process in a pulp and paper mill), and food processing units. They are usually monitored in ambient air near their industrial sources.

Monitoring procedures for mercaptans may be conducted manually or with an automated sequential sampler. When manual (mechanical) techniques are used, samples are collected by bubbling the air through a bubbler (a glass tube with inlet and outlet devices that allow the air to pass through). The bubbler contains a predetermined volume of an absorbing solution and the air passes through at a specific flow rate

(0.6 liter/minute to 2 liters/minute) for a specific period of time up to a maximum of two hours. The absorbing reagent captures the mercaptans present in the sample and a complex is formed. This complex is then diluted and made to react with other chemicals to form a colored complex. The intensity of the color of the complex is measured by means of a spectrophotometer, and the results can directly be related to the amount of mercaptans present in the sample by means of a calibration curve.

Both the sampling rate and sampling time can be adjusted, depending on the expected concentration of mercaptans in the ambient air at the monitoring station. However, these variables should be set so that linearity between the absorbance and concentrations is maintained. Typically, sampling is conducted at least twice a week at any monitoring station.

The equipment for manual methods includes a midget bubbler, an air pump/blower, a flow control device, a membrane-fiber filter, a flow meter, flow calibration equipment, a timer, a thermometer, a barometer, and a spectrophotometer.

The concentration of mercaptans is determined according to the following equation:

$$\text{Mercaptan } (\mu\text{g}/\text{m}^3) = A \times 1000 / V_r$$

Where A = mass of the mercaptan read from calibration curve, mg

1000 = conversion factor, liters/minute

$V_r$  = volume of sample air at standard conditions, liters

The volume of air sampled at standard conditions (25°C, and at one atmospheric pressure) is calculated as follows:

$$V_r \text{ (Liter)} = Q \times t \times \frac{p}{101.3} \times \frac{298.15}{T}$$

Where Q = average flow, liters/minute

t	=	sampling time, minute
p	=	average atmospheric pressure, kPa
T	=	average temperature of air sample, K
101.3	=	pressure of standard atmosphere, kPa
298.15	=	temperature of standard atmosphere, K

**Ammonia.** A colorless, pungent, and suffocating gas, ammonia is generated naturally by the degradation of organic matter. High concentrations may be encountered, however, in urban or industrial areas as a result of emissions from local industrial sources. Likely sources include fertilizer plants, inorganic chemical plants, coke ovens and refineries, as well as the combustion of fossil fuel and the incineration of wastes. High levels of concentration of this gaseous pollutant are harmful to all forms of life.

The presence of ammonia in ambient air is usually monitored by mechanical techniques. The method is similar to that used for SO<sub>2</sub> or NO<sub>x</sub>. A measured volume of sample air is drawn with the help of an air pump (blower) at a specific flow rate (1-2 liters/minute) for a specific period of time (usually one hour). The air stream passes through bubbler/impinger tubes filled with a reagent that reacts with the ammonia in the air sample and forms a complex. This complex is made to react with other chemicals to form a second, colored complex. The intensity of the color is measured colorimetrically against a reagent blank (prepared with the same absorbing reagent), and is directly related to the amount of ammonia present in the corresponding air sample by means of a standard curve. The equipment required for this operation includes a bubbler/impinger tube, a vacuum pump/blower, a flow meter, a glass fiber filter, a timer, a spectrophotometer, and a thermometer.

The amount of ammonia present in the air sample is estimated using the following equation:

$$\text{NH}_3 (\mu\text{g}/\text{m}^3) = \frac{(A - A_0) \times 10^3 \times B_g}{V_r} \times D$$

Where A = sample absorbance

- $A_0$  = reagent blank absorbance  
 $10^3$  = conversion of liters to cubic meters  
 $V_r$  = the air sample volume corrected to 25°C and  
760 mm Hg, liters  
 $B_g$  = calibration factor, mg/unit of absorbance  
 $D$  = dilution factor

## Emission Sources and Inventories

The network of monitoring stations and the raw data compiled from this source are the core of any program to improve air quality. However, other types of information will also be needed, possibly soon after the program is launched. Some of these concepts and supporting data are discussed in this section.

***Inventory of emissions.*** To formulate an effective set of policies and regulations, public officials need a good idea about the types of emissions released into the atmosphere and their major sources. An inventory of emissions can be developed to meet this need. In the ideal case, a specialized system is used to monitor emissions at their source. Unfortunately, this option requires elaborate equipment and highly trained personnel. Such systems currently exist only in a few countries, and even in those instances the data collected is fragmented and must be supplemented with estimates. It is clearly impractical for most developing countries to consider such a sophisticated and expensive alternative. However, construction of a simple version of an emissions inventory is feasible. The approach outlined here focuses on the identification and analysis of hot spots. The results should provide users with enough information to set the priorities for their program and to make tentative decisions on the policies and regulations needed.

The first step in this short-cut approach is to identify the most important point sources of emissions (for example, specific industrial establishments). Statisticians can begin by establishing a cutoff point that distinguishes between large and small establishments. Typically, the

cutoff point would be firms with less than 10 or less than 25 employees. Those with a work force smaller than the cutoff point are excluded from the exercise. Up to 90 percent (and probably more) of all establishments would be eliminated by this criterion, but their omission should not bias the results. Studies in industrialized countries have shown that no more than 10 percent of all establishments are responsible for over 95 percent of air emissions. Furthermore, the big polluters are generally large firms with many workers.

Once the list of large establishments is finalized, analysts should try to determine those that are prone to cause pollution. Potential polluters can be identified with the help of international studies,<sup>23</sup> local expertise, and any previous studies carried out within the country. If possible, all establishments that are potential polluters should be visited. Should their number be too great or too widely dispersed to visit, a subset can be identified. To be representative, the subset should take into account both the size of the firms and the industries involved. Alternatively, the initial inventory can be restricted to a specific geographic area and to a very few types of emissions.<sup>24</sup>

Next, a field survey must be conducted on the basis of the final list of potential polluters. Interviewers may seek information on annual levels of production, raw material usage, energy use, production processes, measures employed to control emissions, and any other relevant information. From the survey, interviewers should be able to carry out a subjective evaluation of emission levels in each establishment. Emission scores are assigned to each establishment, with values ranging from zero (no emissions observed) to 5 (extremely high emissions). A similar evaluation of emission control measures can also be conducted. In that case, assigned values might range from 1 to 5, with the lowest value being given to establishments with satisfactory control measures and the highest to a situation where controls do not exist or are totally inadequate. The

<sup>23</sup> One useful international source is WHO (1993).

<sup>24</sup> For a discussion and some examples of these estimation procedures, see ADB (1999), pages 46-49; and UN Statistical Division (1999), Chapter 2.

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results of these evaluations can be used to identify hot spots—for example, a specific geographic location where the density of industrial polluters is great, a particular establishment responsible for a disproportionate amount of emissions (a point source that is a hot spot), or various industries with high emission potential. Results of the evaluations should be widely distributed so as to provide analysts and policy makers with as much information as possible to combat industrial pollution.

***Inventory of depositions.*** Still another component in a fully developed system for monitoring air pollution would be an inventory of depositions. The methodology for estimating wet deposition is rather well developed, but the same is not true for the calculation of dry deposition. The latter depends crucially on variables such as deposition velocity, the distribution of pollutants between the aqueous and dry phase, and the reliability of measurement methods. For these reasons, very few programs to monitor air quality consider dry depositions. A deposition inventory can be a valuable adjunct to a program for monitoring air quality, but it requires considerable expertise and should probably receive a lower priority than an inventory of emissions. It is recommended that countries at an early stage in the program of environment statistics defer development of this tool until a time when more experience has been accumulated.

***Categories of emission sources.*** The practice of identifying emission sources by category is a common one, though it has no direct relevance to the data on air quality obtained via the system of monitoring stations. The convention is helpful, however, when readings for certain parameters exceed quality standards. In such a case, environmental managers will need to refer to the emissions inventory, and their task is made easier if records distinguish between different categories of emission sources.

At the most general level, sources of pollution can be described as stationary or mobile. Many stationary sources are associated with industrial activities. Within the industrial sector, two types of emissions from stationary sources are identified.

- (i) Emissions resulting from the combustion of fossil fuels. The industrial activities producing these emissions are usually

intended to generate power or heat. Compounds emitted include  $\text{SO}_2$ ,  $\text{NO}_x$ , SPM, CO, VOC, and  $\text{CO}_2$ . Both the release and deposition of these compounds depend on the fuel used, the specific production process, and the existence of any cleanup technology, if any.

- (ii) Process emissions associated with production processes. Many production processes require the physical or chemical transformation of materials. Others involve auxiliary substances that are used either for cleaning or for facilitating a chemical reaction. Industrial processes may release a large number of compounds into the air. The compounds may be associated with an input for the process, a chemical reaction occurring at an intermediate stage, or the final product itself. Because of these characteristics, the task of monitoring process emissions is more complicated than that of monitoring the combustion of fossil fuels.

A third stationary source exists in the household sector. Many households use biomass, coal, wood, kerosene or other "dirty" fuels for heating and cooking. The resultant pollution can be substantial if a large number of households in a city or urban area rely on these energy sources. The emissions, however, are much closer to the ground than those from stationary industrial sources and therefore have a more localized impact. Household emissions of combustible fuels are generally treated as part of the environment statistics of human settlements.

In addition to the two stationary sources in the industry sector, there is one important mobile source of emissions: the combustion of fossil fuels when transporting people and freight. The main emissions from motor traffic include  $\text{SO}_2$  and SPM (both originating mainly from diesel fuels),  $\text{NO}_x$ , CO, VOC, lead (from leaded gasoline), and  $\text{CO}_2$ . Motor vehicles are concentrated in urban areas and, like households, their emissions are at ground level. Therefore, the pollution associated with transportation tends to be localized. If traffic congestion is substantial, emissions will be greater owing to frequent stops, accelerated starts,

and idling motors. The poor quality of fuel is another factor contributing to pollution. Diesel fuels that are not desulfurized and leaded gasoline with high benzene content are especially dirty fuels. The amount of pollution attributed to motor traffic will also be higher if vehicle maintenance is generally poor, or if the vehicle fleet is relatively old.

### Estimating Air Emissions

Air emissions come from many sources and no single method of estimation is possible. However, the task is simplified somewhat when the focus is on individual categories of emissions. The estimation procedures that may be employed for different categories of emissions are described in this section.

**Emissions from fossil fuels.** The combustion of fossil fuels is a relatively homogeneous process since the fuels and technologies for combustion and cleanup are limited. If energy statistics are available, figures on fuel usage can be derived. Preliminary estimates of emissions can then be calculated using WHO emission factors (WHO 1993) or local emission factors, if these are available. At this point, the estimates should be adjusted to take account of cleanup technologies. The results of this procedure can be compared or combined with data acquired from actual measurements. If data on the maximum allowed emissions is available from records of emission permits, this source can also be used to check the estimates.<sup>25</sup> The accuracy of the estimation procedure will vary substantially, depending on the precision of the data on which the estimates are based. For SO<sub>2</sub>, the sulfur content of the fuel is the most important determinant. In the case of NO<sub>x</sub>, the combustion technology is the critical factor. In general, emission factors are less accurate than data on fuel consumption.

<sup>25</sup> Swedish officials use the maximum allowed emissions to compute the emissions of SO<sub>2</sub> and NO<sub>x</sub> for all but the largest combustion plants. This approach may result in overestimates in Sweden, but in many developing countries the same procedure may yield an underestimate since actual emissions often surpass the allowed levels.

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An example of the procedures used to estimate industrial emissions is presented in Table 4.5. The data refer to the city of Dhaka. At the time of the study, about 400 industrial establishments were registered. A far greater number was not registered, for most of these establishments either were too small to have significant emissions or were not regarded as major air polluters. A review of the register revealed that only 32 establishments were at least of medium size. These firms were widely dispersed around Dhaka. Most were in industries such as textiles and clothing, printing, beverages, and chemical processing, and their contribution to air pollution was primarily from boiler stacks. Because all boilers and furnaces used natural gas as fuel, the only significant emissions from these industries were assumed to be  $\text{NO}_x$ , CO, and VOCs.

Based on average boiler size and estimated steam production, gas consumption was computed, and from these figures emissions of CO and VOC were derived. Metallurgical, glass, and refractory establishments also used gas furnaces exclusively. In these operations, some  $\text{SO}_2$ , NO, and a considerable amount of SPM would be emitted. Estimates of average emissions per day per furnace were assumed for metallurgy and related industries. Finally, the many small-scale units around the city were assumed to contribute an amount of air pollution equal to the sum of emissions from medium-scale units.

Based on these calculations, analysts were able to identify the major industrial polluters and estimate industrial emissions. They concluded that industrial pollution was probably less than that attributed to vehicular traffic. The use of a relatively clean fuel (natural gas), coupled with the fact that industrial emissions are released at a much greater height than traffic emissions, were two considerations supporting this conclusion.

**Process emissions.** As noted in the preceding section, a large number of different compounds are released into the air by industrial processes. A careful review of production statistics will yield no more than partial information on this subject, since production methods, cleanup technologies, and operating conditions are also relevant. Generally, countries that have only recently begun to compile environment statistics should probably postpone the development of an inventory of process emissions for at least a few years.

**Table 4.5: Estimates of Industrial Emissions in Dhaka, 1992  
(no. of units and kilograms of emissions per day)**

Item	Medium-Size Units		Total	Small-Scale Units	Total Dhaka
	Textiles <sup>a</sup>	Metallurgical <sup>a</sup>			
Units	14	18	32	>300	>330
SPM	–	360	360	360	720
CO	3,500	900	4,400	4,400	8,800
HC	3,500	900	4,400	4,400	8,800
NO <sub>x</sub>	–	1,800	1,800	1,800	3,600
SO <sub>2</sub>	–	180	180	180	360

<sup>a</sup> Includes related industries.

Source: Bangladesh Department of Environment (1992).

Once a country is ready to proceed, it will be critical to determine which types of emissions deserve priority. Although thousands of chemical compounds are released into the air, only a handful are of national importance and just a few assume local significance. A careful screening of production statistics would be the first step in this exercise. WHO (1993) has produced a list of process emissions identified according to the International Standard Industrial Classification (ISIC) and this information should be helpful in the screening.<sup>26</sup>

The types of emissions and not the volumes are the overriding feature in assigning priorities. Toxic substances can have effects at a very low level, while more common emissions such as NO<sub>x</sub> are released in great quantities but have only moderate effects. The list of special compounds in Table 4.6 may be helpful in compiling a preliminary list of substances to be included in the inventory. Other lists produced by OECD and national agencies are also available and can be consulted. However, users should bear in mind that some chemicals and toxic substances that are now banned in industrialized countries may still be used or even produced in their own country.

<sup>26</sup> Additional information can be found in WHO (2000b).

**Traffic emissions.** Some problems encountered when estimating traffic emissions are the amount and variety of pollution sources and their mobility. Emissions also vary depending on the types of vehicles in use, their age and state of maintenance, the type and quality of fuel, driving patterns, and other factors. Analysts will need to start by determining the composition of the active vehicle population. Usually, such information can be obtained from official registrations systems for license plates, car ownership, or insurance.<sup>27</sup>

**Table 4.6: Compounds to Consider in an Inventory of Process Emissions**

Arsenic	Coke oven emissions	Perchloroethylene
Asbestos	Ethylene dibromide	Polycyclic organic matter
Benzene	Ethylene dichloride	Radionuclides
Beryllium	Ethylene oxide	Trichloroethylene
1,3 Butadiene	Formaldehyde	Vinyl chloride
Cadmium	Gasoline vapors	Vinylidene chloride
Carbon tetrachloride	Mercury	
Chloroform	Methylene chloride	

In addition to the statistics gathered on vehicle population by category, the most important set of data is the set of emission factors by driving mode, by vehicle age, and type. Standardized estimates of emission factors have been published and can be used, but locally derived estimates and road measurement values are preferred.<sup>28</sup> An example of one set of emission factors for metropolitan Manila is shown in Table 4.7. Using

<sup>27</sup> The system should be checked to verify that it is up-to-date. If not, further adjustments will need to be made.

<sup>28</sup> Characteristics such as maintenance practices, driving patterns, and the age of the vehicle population vary widely from country to country and their effects will be reflected in the values of emission factors. The appropriateness of standardized factors can be questionable in some instances.

**Table 4.7: Emission Factors in Metropolitan Manila (g/km)**

Vehicle type	CO	HC	NO <sub>x</sub>	Sulfur	Lead	Particulates
Car	49.5	6.0	2.7	0.011	0.073	0.1
Utility vehicle (gas powered)	60.0	6.0	2.7	0.014	0.092	0.12
Utility vehicle (diesel powered)	2.5	0.7	1.4	0.115	0	0.9
Taxi	1.9	0.65	2.0	0.081	0	0.6
Jeepney	2.5	0.7	1.4	0.121	0	0.9
Truck	12.4	3.7	12.5	0.374	0	1.5

Source: ADB (1995).

an approach similar to that described here, and based on the emission factors given in the table, analysts determined that trucks and buses accounted for 41 percent of all emissions in Manila, jeepneys and taxis contributed 24 percent and utility vehicles were responsible for 20 percent.

To conclude, three types of emission inventories have been described in this section. None of this information may be available in countries that only recently launched an environment statistics program. However, these inventories are important components of any program and their development should be considered once sufficient experience has been gained. The highest priority should probably be assigned to industrial emissions, followed by traffic emissions.