



GAP Forum Air Pollution Monitoring Manual

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1. Introduction

In recent decades, the combination of the growth of cities around the world, increased use of vehicles, rapid industrialisation, and deficiencies in both planning and environmental regulations, has led to increasing levels of air pollution and consequent health and environmental impacts in many countries. Observed levels of a number of important air pollutants- including fine particulate matter (PM), sulphur dioxide (SO₂), nitrogen dioxide (NO₂), ozone (O₃) and lead (Pb)- often reach magnitudes that are considered to be a threat to human health. Although ambient concentrations of certain air pollutants (such as SO₂, coarse particles and Pb) are decreasing in many countries, levels of other gaseous pollutants such as NO₂ and fine particles are stable or even increasing over time.

The rationale for this Air Pollution Monitoring Manual is to introduce people with little experience and a low budget for air quality monitoring to the best and least expensive monitoring practices which still meet their monitoring and data quality objectives. The target audience of the manual are policy advisors and managerial staff in developing countries.

1.1 What is air pollution

Outdoor (or ambient) air pollution can be defined as ‘the presence of contaminants/pollutants in the outdoor atmosphere in such concentration and of such duration which may adversely affect human health, the environment, materials, and have economic impact’. Indoor air pollution can be defined as ‘the presence of contaminants/pollutants in the indoor atmosphere in such concentration and of such duration which may adversely affect human health and have economic impact’.

1.2 Sources of air pollution

Pollutants in the atmosphere may be solids, liquids, and/or gases. Sources can be classified as

- Naturally occurring processes such as volcanic eruptions, sand storms, vegetation fires, and
- Man-made activities such as transport operations, industrial manufacturing, construction, leisure and other socio-cultural activities.

Major sources of air pollution are summarized in Table 1.1.

Table 1.1: Major sources of air pollutants

Source type	Source	Causal action
Natural	Volcano eruption	Release of solid particles, gases and heat waves
	Sand storm	Dust particles spread through wind circulation around the earth
	Vegetation fire	Smoke from wildfire or forest management
	Plant Pollen	Spread of plant pollen spread through wind motion
	Sea spray	Liquid droplets spread through wind near coastlines
Man-made	Transport	Combustion of petrol/diesel and generation of particles and gases
	Power generation	Release of particles and gases
	Industry	Manufacturing and processing of steel, non-iron metals, textiles, refining of petroleum, handling of materials
	Construction	Particle pollution due to material handling and other associated activities
	Agriculture	Emissions from ploughing and use of fertilizers, pesticides and insecticides
	Leisure activity	Emissions from motor racing, snowmobiles, private planes, lawn mowers and other garden appliances, etc.,
	Domestic	Burning of solid organic materials indoors such as coal, wood, dung, agricultural residues

1.3 Classification of air pollutants

Air pollutants can broadly be classified according to the

- State of matter (particulate, gaseous pollutants);
- Origin of pollutants (primary, secondary pollutants);
- Chemical composition (organic, inorganic pollutants).

Particles can be solid or liquid and composed of inert or chemically reactive materials of size ranging from 2 nanometres (nm) to 500 micrometres (μm). They include aerosols (suspended particulate matter, SPM), dust, smoke, soot, fumes, mist, fog, and haze. Particles are distinguished as coarse, fine and ultrafine. Coarse particles are those of size between 10 and $2.5 \mu\text{m}$; fine particles are those of size less than $2.5 \mu\text{m}$ (denoted as $\text{PM}_{2.5}$) and ultrafine particles are those of size less than $0.1 \mu\text{m}$.

Gaseous pollutants include gases and vapours such as sulphur oxides, oxidized and reduced nitrogen, oxygen, and organic compounds. Major pollutants in the urban air are SO_2 , nitric oxide (NO), nitrogen dioxide (NO_2), ozone (O_3), carbon monoxide (CO), and the greenhouse gas carbon dioxide (CO_2).

Primary pollutants are those directly emitted into the atmosphere from the source; secondary pollutants are those formed due to the interaction of one or more primary pollutants or as a results of a reaction with atmospheric constituents (e.g. O_3 formation).

Organic pollutants include methane and non-methane hydrocarbons, aldehydes, volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs).

1.4 Health effects of air pollution

In its World Health Report 2002, the World Health Organisation (WHO) has estimated the global burden of disease due to 14 factors including outdoor, indoor and workplace air pollution (WHO, 2002a). According to this report about three million people die prematurely each year due to air pollution, most of them due to indoor air pollution from open stove cooking and heating. In 2006, WHO estimated the national burden of disease due to outdoor

and indoor air pollution for all its Member States (WHO, 2006a). The results of these estimates in terms of years of life lost in the six WHO regions are shown in figure 1.1.

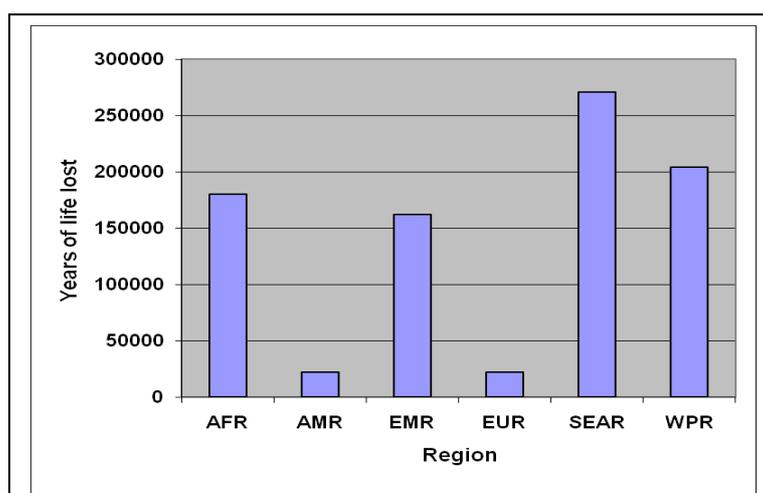


Figure 1.1: Years of life lost due to outdoor PM air pollution in the WHO six regions

Source: WHO 2006a; AFR=African region; AMR= American region; EMR Eastern Mediterranean region; EUR= European region; SEAR= South East Asian region; WPR= Western Pacific region

Outdoor air quality monitoring is of fundamental importance in identifying the extent and sources of any pollution problem; it also provides the basis for developing appropriate control strategies as well as assessing their success. Indoor air quality monitoring is necessary to identify the success of measures to reduce emissions by use of cleaner fuels and improved stoves.

Health effects are the primary reason for work to improve air quality. Health effects of air pollution only occur where people live and are exposed. In order to be able to assess the effects of air pollutants on health, reliable estimation of exposure to indoor and outdoor air pollution is necessary.

The health impacts of air pollutants are numerous and varied and can become manifest in any compartment of the human body. Compartments affected include the respiratory system, immune system, skin and mucous tissues, sensory system, central and peripheral nervous system, and the cardiovascular system (Schwela, 2009).

Health effects of air pollution on the **respiratory system** include acute and chronic changes in pulmonary function, increased incidence and prevalence of respiratory symptoms, sensitisation of airways to allergens, and exacerbation of respiratory infections such as rhinitis, sinusitis, pneumonia, alveolitis, and legionnaires' disease. Principal agents for these health effects are the combustion products PM (PM₁₀, PM_{2.5}), O₃, SO₂, NO₂, and CO.

- PM varies widely in terms of size, blackness, chemical composition and its potential for health effects. The larger particles are trapped or removed by the body's own biological defence systems. Smaller particles (less than about 10 µm in diameter) can penetrate deeply into the lungs, resulting in irritating or obstructive effects. Particles below 2.5 µm aerodynamic diameter have been associated with cardio-respiratory morbidity and mortality (WHO, 2006). Some constituents of fine particulate matter such as diesel smoke may be carcinogenic (WHO, 1996).
- Short-term exposures to O₃ can impair pulmonary function and produce transient obstructive pulmonary alterations, particularly in people with asthma and allergic rhinitis.

O₃ enhances airway responsiveness in both healthy individuals and asthmatics. Short-term exposure to O₃ increases morbidity, school absenteeism, hospital admissions or emergency department visits for asthma, respiratory tract infections and exacerbation of chronic airway diseases. In the elderly, short-term exposure to O₃ can increase mortality (WHO, 2006b). Long-term exposure to O₃ can induce significant changes in airways at the level of the bronchioli.

- High concentrations of SO₂ can irritate the respiratory system, induce coughing or result in usually reversible changes in lung function. While an association between short-term SO₂ exposure and mortality could not be established, positive associations for cardiovascular hospital admissions were found. Long-term exposure to SO₂ appeared to show a positive and significant association with all-cause mortality after adjustment for other air pollutants, including fine particles and sulphates (WHO, 2006b).
- NO₂ is also a respiratory tract irritant, and is toxic at high concentrations. A consistent association between NO₂ exposure and hospital admissions and emergency department visits for asthma in children has been established after adjusting for PM and O₃. There is evidence to suggest an association between long-term NO₂ exposure and the incidence of asthma in children, and reduced lung function (WHO, 2006b).
- CO has a strong affinity for haemoglobin, the oxygen-carrying substance in blood. When oxygen is displaced by CO, it can progressively lead to oxygen starvation and, can exacerbate cardiovascular diseases and myocardial infarction, and CO poisoning can lead, in extreme cases, to death (WHO, 2000a).

In addition, indoor air pollutants—fine PM from environmental tobacco smoke (ETS), formaldehyde, and infectious organisms—can also act as important agents causing respiratory effects.

Effects of air pollution on the **cardiovascular system** develop through reduced oxygenation and result in increased incidence and prevalence of cardiovascular diseases, myocardial infarction, and consequent increase in mortality caused by cardiovascular diseases. Principal agents are CO, PM, and ETS.

Health effects of air pollution on immune system allergies manifest themselves in exacerbation of allergic asthma, allergic rhino-conjunctivitis, extrinsic allergic alveolitis/hypersensitivity pneumonitis, and can produce permanent lung damage in sensitised individuals including pulmonary insufficiency. Principal agents are known to be outdoor allergens and indoor air agents such as house mite dust, cockroaches, organisms living in the pelt of pets, insects, and moulds in high humidity environments. Multi-centre studies have shown different spatial patterns of allergic disease (e.g., asthma, rhinitis, and eczema) as well as allergic hyper-sensitisation. These variations cannot be reconciled by geographical differences in allergen exposure since the major aeroallergens are widespread.

Pollens can trigger an allergic response in the airways of susceptible asthmatics, causing inflammation and consequent narrowing. At high concentrations air pollutants can enhance the effect of some pollens. Air pollution may also affect the concentration of pollens (EP, 2010).

Health effects of air pollution on the skin and on mucous tissues (eyes, nose, throat) are mostly irritating effects. Primary sensory irritations include dry—sore—throat, tingling sensation of nose, and watering and painful eyes. Secondary irritation is characterised by oedema and inflammation of the skin and mucous membranes up to irreversible changes in these organs. Principal agents include volatile organic compounds, formaldehyde and other aldehydes (e.g., acetaldehyde, acrolein) and ETS.

Sensory effects of air pollution include nuisance and annoyance reactions caused by perception of air pollutants through sensory organs. VOCs, formaldehyde and ETS can act as principal agents.

Effects of air pollution on the central nervous system manifest themselves in damage of the nerve cells, either toxic or hypoxic/anoxic. Principal agents are VOCs (acetone, benzene, toluene, formaldehyde), CO, lead (Pb) and pesticides. In infants and young children, neuro-physiological changes caused by Pb can result in developmental retardation and irreversible deficiencies.

Carcinogenic effects of air pollution are associated with lung cancer, skin cancer, and leukaemia. Principal agents for lung cancer have been identified as arsenic, asbestos fibres, chromium, nickel, cadmium, polycyclic aromatic hydrocarbons (PAH), trichloroethylene, ETS, and radon. Benzene is known to produce leukaemia, and ultraviolet radiation is a causative agent of skin cancer. A difficult and largely unresolved question is that of synergism among the different carcinogenic compounds and between carcinogenic and non-carcinogenic agents.

The health impacts of lead are especially serious in children because lead affects the body during the crucial development phases. Children are known to develop learning disabilities and suffer from intelligence quotients decrease. In most countries lead in petrol has now been phased out. Lead is, therefore, only a major challenge in and around lead-processing industries.

1.5 Ecotoxic effects

In order to consider the ecological effects of major pollutants it is necessary to formulate criteria for the assessment of the effects of air pollutants on the natural environment. This section focuses on the ecological effects of ozone, nitrogen dioxide (and other nitrogen compounds including ammonia) and sulphur dioxide (including sulphur and total acid deposition), which are thought to be currently of greatest concern. A number of other atmospheric contaminants such as suspended particulate matter and gaseous and particulate fluorides are also known to have ecological effects but are not considered here. The ecological effects of the three pollutants are characterised as follows.

Ozone. Short-term O₃ exposure of broad-leaved plants may induce acute injury symptoms such as necrosis, chlorosis (whitened areas of dying leaf tissue), bleaching, bronzing, flecking and stippling. On conifers, common symptoms of short-term exposure include necrosis, mottling and banding. Long-term exposures may result in visible symptoms such as chlorosis, premature senescence and leaf abscission, and in growth reduction. Growth reduction can result in crop yield losses, reduction of annual biomass increments for forest trees and shifts in species composition (Emberson et al., 2003).

O₃ exposure is expressed as the sum of all 1-hour mean concentrations above a cut-off concentration of 40 ppb (80 µg/m³). The cut-off concentration is used to calculate an exposure index that provides significant linear relationships between O₃ exposure and plant response for a number of species and hence to the degree of risk to sensitive vegetation. The index (referred to as the “Accumulated exposure Over a Threshold of 40 ppb”, AOT40, in units ppm-h) is calculated during those daylight hours when radiation is higher than 50 W/m² for a 3-month growing season in the case of crops and semi-natural vegetation, or a 6-month growing season for trees.

Nitrogen oxides (NO_x). The biological effects of nitrogen oxide (NO) and NO₂ differ substantially and it is not certain which compound is more toxic. Short-term exposure to high concentrations and prolonged exposure to lower concentrations of NO_x can suppress plant

growth. Even if growth is stimulated by long-term exposure to low NO_x concentrations Short-term exposure to very high NO₂ concentrations can lead to chlorotic areas on leaves associated with necrotic patches. Synergistic effects have been observed for simultaneous exposures of plants to NO₂ and SO₂ or O₃ and NO₂.

Sulphur dioxide. Long-term exposure to low SO₂ concentrations can cause reduction in growth and yield and change plant sensitivity to other environmental stresses such as heat, cold and pathogens. Short-term exposure to high SO₂ concentrations around smelters have caused chlorosis of leaf tissue.

1.6 Need for ambient air quality monitoring

The capacity of the earth's atmosphere to clean itself is limited in areas with high air pollutant emissions, low ventilation rates due to topological/meteorological conditions or otherwise toxic emissions beyond the assimilating capacity from various pollution sources. Air pollution is a major problem in urban areas of developing countries, where all kinds of pollution sources are present. Therefore, there is an urgent need to protect humans, animals, vegetation and materials from damaging exposure to air pollution. Ambient air quality monitoring (AAQM), therefore, is necessary to first define the nature and severity of the problem and to help develop an effective strategy for air quality management (AQM).

1.7 Status of AAQM in developed and developing countries

Currently, in most developed countries fully automated systems for AAQM are used, having simultaneous visual display and auto-transmittance facility. AAQM programmes in developing countries have severe resource and infrastructure constraints. Often such constraints are the sole factor for any ultimate decision on monitoring network configuration and the minimum local data needs. Therefore, AAQM systems have to be designed very carefully to meet the desired objectives with optimal utilization of available resources.

1.8 Air quality standards

An air quality standard (AQS) is a promulgated limit placed on an ambient air pollutant concentration for a defined period of time. As such, an AQS characterizes the enforceable level of a pollutant (or a class of pollutants) in the atmosphere. An AQS defines the amount of exposure permitted to the general population and/or to the environment.

An air quality guideline value (AQG) is a recommendation for an air pollutant concentration, which has a negligibly low risk for adverse impacts on human health and/or the environment. An AQG value is based solely on public health, toxicological and/or environmental studies. AQGs do not consider economic, social, technical and political issues. In contrast, AQSs are not based exclusively on the studies used for deriving the AQG values but have taken into consideration a broad range of economic, social, technical and political requirements.

In Table 1.2 the WHO AQG values are presented (WHO, 2006).

Table 1.2: Some AQG values for the protection of human health

Pollutant	Averaging time	Guideline value [$\mu\text{g}/\text{m}^3$]	Reference
Total suspended particulate matter (TSP)	1 year	60-90	WHO, 1979
	24 hours	100-150	
PM ₁₀	1 year	50	WHO, 2006b
	24 hours	20	
PM _{2.5}	1 year	25	
	24 hours	10	
SO ₂	24 hours	20	
NO ₂	1 year	40	
	1 hour	200	
O ₃	8 hours	100	
CO	8 hours	10,000	WHO, 2000a
	1 hour	30,000	

For ecotoxic effects of air pollution two types of criteria have been defined by WHO (2000a): *critical level* and *critical load*.

Critical level is the concentration of air pollutants above which direct adverse on receptors such as plants and ecosystems may occur (according to extant knowledge).

Critical load is a quantitative estimate of an exposure, in the form of deposition, to one or more pollutants below which significant adverse effects on specified elements of the environment do not occur (according to extant knowledge).

“Critical levels relate to direct effects on plant physiology, growth and vitality, and are expressed as atmospheric concentrations or cumulative exposures over a given averaging time. Typically, critical levels are based on effects observed over periods of from one day to several years. Critical loads relate to effects on ecosystem structure and functioning, and are expressed as annual depositions of mass or acidity. Typically, critical loads relate to the potential effects over periods of decades. In the case of sulphur and nitrogen compounds, critical levels can be directly related to critical loads when the deposition velocity for a given vegetation type is known. Nevertheless, while critical levels provide effects thresholds for relatively short-term exposures, and are not aimed at providing complete protection of all plants in all situations from adverse effects, critical loads provide the long-term deposition below which we are sure that adverse ecosystem effects will not occur. Both critical levels and critical loads may be used to indicate the state of existing or required environmental protection” Table 1.3 shows the WHO guideline values for the protection of plants (WHO, 2000a).

Table 1.3: Guideline values for the effects of ozone, nitrogen compounds and sulphur dioxide (WHO 2000a)

Compound	Vegetation category	Guideline value AOT40 [ppm-h]	Time period	Constraints/remarks
O ₃	Crops (yield)	3	3 months	
	Semi-natural vegetation			
	Crops (visible injury)	0.2	5 days	Humid air conditions (VPD < 1.5 kPa)
		0.5		Dry air conditions (VPD > 1.5 kPa)
	Forests	10	6 months	
		Guideline value [µg/m³]		
NO _x	All vegetation	75	24 hours	
		30	1 year	NO _x =NO+NO ₂ [ppb], expressed as NO ₂
NH ₃		230	24 hours	
		8	1 year	
SO ₂	Agricultural crops	30	1 year and winter mean	Lower value if annual mean of temperature above 5°C is less than 1000°C
	Forests and natural vegetation	15-20		
	Lichens	10	1 year	
Sulphate particles	Forests	1		

1.9 Design requirements of AAQM

The effectiveness of an air quality management programme can only be determined through a regular and accurate assessment of air quality. For setting up a meaningful AAQM system, answers to the following questions are imperative:

- Why monitor air quality?
- What air quality indicators should be monitored?
- Where should air quality be monitored?
- When should air quality be monitored?
- How should air quality be monitored?
- What are the infrastructural support, resources and institutional requirements, etc.?

These questions are answered in the subsequent sections of this Manual.

2. AAQM Objectives

2.1 Why monitor

The first step in designing and implementing any AAQM system is to define its overall objectives. Most of the AAQM programmes are normally designed to provide for the national, regional or local scale needs for one or more of the following objectives:

- To establish the general background concentration levels;
- To test compliance with air quality standards;

- To observe long-term pollution trends;
- To establish exposure-response and/or cause-effect relationships regarding the risk to human health, animals, crops, ecosystems;
- To assess the impact of significant sources or source categories on the ecosystem;
- To develop urban land use and/or transportation plans;
- To develop control strategies and regulations;
- To evaluate the effectiveness of control strategies;
- To activate emergency control procedures for episodic conditions;
- To develop, calibrate and/or validate dispersion models.

Overall objectives need to be clearly defined for any monitoring system. Setting diffuse, overly restrictive or ambitious objectives may result in cost-ineffective programmes with poor data utility. In such circumstances, it will not be possible to make optimal use of the manpower and resources committed to air quality monitoring.

2.2 Quality control/quality assurance

Whatever the objectives— whether for health impact assessment, to meet local or national objectives, assessing traffic or industrial impacts, planning, policy development or providing public information - measurements will need to be accurate and reliable if they are to prove useful.

This is why quality assurance and control (QA/QC) is a key component of any monitoring programme. Without this, measured data will not provide a sound basis for assessment of population health effects of air pollution or for effective air quality management; as a result, any investment of money, time and effort made in monitoring will have been wasted.

Proper QA/QC is also essential in ensuring the comparability of measurements made at different monitoring sites. QA/QC is therefore a basic tool in ensuring that data within a network of sites are *harmonised*. The conditions for the quality control (calibration) of the measurements are often defined in the Data Quality Objectives (DQO). These state how accurate and/or precise the data should be and also the required availability of data before they can be used in further statistical evaluation.

A properly designed and implemented QA/QC programme should cover all aspects of network operation, ranging from system design and site selection through equipment selection, operation, calibration and maintenance to data management and validation. Such a programme therefore covers the complete sequence of activities, which assures that a measurement meets defined standards of quality with a stated level of confidence.

Essentially, quality assurance refers to the overall management of the entire process leading to a defined quality of the data product; quality control refers to the activities undertaken to obtain a specified accuracy and precision of the measurement. Before embarking on an AAQM programme, it is necessary to draw up a detailed quality assurance plan covering all aspects of quality assurance and control. The quality assurance programme will cover all the important pre-measurement phases of monitoring, ranging from definition of data quality objectives, and system design and site selection through to equipment evaluation, selection and deployment, and operator training. Quality control functions will cover directly measurement-related activities including network operation, calibration, data handling, review and training.

2.3 What to monitor

If one goes by the whole list of air pollutants with proven adverse effects, then the number of monitoring parameters shall be exorbitant. However, all air pollutants may not be relevant for certain AAQM programmes. Therefore, only few air pollutants are chosen for any given area considering their potential for adverse effects on human health, animals, natural vegetation, agricultural crops or the ecosystem. In general, it is necessary to first focus on those pollutants, for which AQS or AQG exist.

In cases where AQSs are yet to be promulgated in a country standards for other countries or areas may not be applicable, as the pollutants of concern may vary from one region to another even within the same country due to the characteristics of local sources of the area concerned. Before a final selection of what to monitor is made, special short-term pilot studies of cross-sectional nature could help define the local problems. For inter-regional comparison purposes it is desirable to have defined a set of basic pollutants for all the regions in consideration.

This section provides a brief review of some of the major air pollutants of concern. Further detailed information is available from a variety of sources, including the WHO Guidelines for Air Quality (WHO, 2000a; b; 2006b), the Environmental Health Criteria Series of the International Programme for Chemical Safety (e.g. WHO 1997; 1999a) and review articles (Holgate et al., 1999).

Particulate Matter (PM)

This term covers the range of coarse, fine and ultra fine solid or liquid particles dispersed in the atmosphere, as opposed to larger size fractions, which rapidly settle out due to gravity. PM is monitored as total suspended particles (TSP), particles of diameter less than 10 μm (PM_{10}) or less than 2.5 μm ($\text{PM}_{2.5}$). Together with SO_2 , PM was the first pollutant to be widely studied in urban areas.

PM can be produced from a wide variety of sources. These include coal combustion, diesel engines, construction and industrial activity, secondary aerosols (formed from ammonia, sulphur and nitrogen oxides by reaction in air), as well as natural sources such as soil blow-off and plant pollen. Particulate matter concentrations in urban areas are strongly dependent on source types and emission patterns. Consequently, concentrations may show considerable spatial variability within cities and great diversity from city to city.

Sulphur Dioxide (SO_2)

This pollutant is a colourless acidic gas with a choking taste. Natural emissions account for approximately 20-25 per cent of all atmospheric SO_2 . Man-made SO_2 is produced by the combustion of sulphur components which are a natural constituent of coal and oil. Coal burning accounts for 50 per cent of annual global SO_2 emissions with oil and diesel burning contributing a further 25-30 per cent (UNEP, 2009).

Ambient concentrations of SO_2 are usually highest in temperate cities where there is significant use of coal and/or oil for domestic space heating. The move towards cleaner fuels or heating techniques has resulted in very substantially lower pollutant levels in Europe and the United States over the last 30-40 years (e.g. US EPA, 2010a).

Ambient concentrations of SO_2 are usually highest in and around industrial areas. In some parts of Europe, North America and China, anthropogenic SO_2 emissions lead to acid precipitation; this has been an important concern in these areas over the past decades (Huang et al., 2009; Yu-Zhen Cao et al., 2009; US EPA, 2008; SEPA 2005; Ito et al., 2002; Topcu et al., 2002; Marquardt et al., 2001; Heuer et al., 2000; Avila & Alarcon,

1999; Almomani et al., 1998; Sanusi et al., 1996; Smirnioudi & Sidkos, 1992; Barrie & Hales, 1984; Galloway et al., 1984; Cowling, 1982;).

Nitrogen Oxides (NO_x)

Nitrogen oxides are emitted from natural and man-made sources in nearly equal quantities, but whereas natural emissions tend to be equally distributed world-wide, man-made sources are concentrated in centres of population (WHO, 1997). The most important oxides of nitrogen in urban atmospheres are nitric oxide (NO) and nitrogen dioxide (NO₂). Of the two species, NO₂ has the more significant health and ecosystem impacts.

The major outdoor sources of NO₂ in urban areas are fuel combustion in motor vehicles, power generation, heating plants and industrial processes. Relatively limited quantities of NO₂ are emitted directly from these sources; most NO₂ in the atmosphere is subsequently formed by oxidation of nitric oxide (NO) emissions. Concentrations in urban areas are usually dominated by traffic emissions, being highest in central areas and close to major roads.

NO₂ is also involved in the formation of photochemical smog, acid rain and secondary formed particles.

Carbon Monoxide

Carbon monoxide is produced by the incomplete combustion of fossil fuels or organic materials. Its major outdoor source is motor traffic. The spatial distribution of CO concentrations in urban areas is strongly traffic-dependent, and will therefore tend to follow that for NO₂. Levels are highest at the kerbside but decrease rapidly with increasing distance from the road (WHO 1999a).

Ozone

Outdoor ozone is a secondary air pollutant, formed in the troposphere from atmospheric reactions between oxides of nitrogen and volatile organic compounds (VOCs) in the presence of sunlight. The spatial distribution of ozone is substantially different from that of other common urban air pollutants. Since its formation in the atmosphere can occur over time scales of hours to days, concentrations are temporally and spatially decoupled from NO_x and VOC emissions. Moreover, chemical scavenging by NO_x emissions in near-source areas results in highly variable ozone concentrations over small spatial scales. There is a lack of measured data on such variations, though urban concentrations may be expected to be lowest where corresponding levels of other primary pollutants such as NO_x and CO are highest. Ozone concentrations should be measured outside the city, in background areas, as regional ozone concentrations may indicate the formation of NO₂ inside the city.

In practice, exposure of the population to ozone will tend to be higher in suburban rather than central parts of cities, and in areas downwind of major populated or industrialised regions. Levels may also be high in cities with basin-type topographic situations such as Mexico City, Athens and Los Angeles. Ozone reacts readily with biological receptors; it may cause eye, nose and throat irritation, acute effects on the respiratory tract and breathing difficulties (WHO, 2006).

In addition, it may be required to determine certain other toxic components such as heavy metals (As, Cd, Ni, Pb); cations (Al³⁺, H⁺, NH⁴⁺, etc.), anions (SO₄²⁻, NO₃⁻, etc.) present in rain water, PAHs like benzo[a]pyrene present in aerosol samples, and VOCs like benzene.

Once the pollutants from different sources are released into the atmosphere, their dispersion, removal or transformation in the ambient air is governed by meteorological and topographical factors. Meteorological factors include wind speed, wind direction, temperature, humidity, rainfall, atmospheric stability conditions, solar radiation, etc. Topographical factors include irregularities of the Earth's surface such as mountains and forests.

Therefore, consideration should also be given to the monitoring of certain important meteorological parameters and classifying the terrain. In many situations, however, a minimum set of meteorological data can be used from the nearest meteorological station such as monitored by a meteorological department or at an airport.

2.4 Where to monitor

In cities, monitoring is usually undertaken at selected sites, rather than at points on a grid. Sites should be representative of specific location types covering, for example, characteristic central urban, industrial, residential, population-exposure, commercial or kerbside areas. Appropriate site selection will involve consideration of a variety of possible data inputs, including the following:

Overall Monitoring Objectives. These will usually determine appropriate types of target area for study. For example, traffic-oriented monitoring may involve kerbside or near-road sites, whilst epidemiological studies will emphasise background, suburban or city-centre population exposure locations.

Sources and Emissions. Compilation of emission data is usually an important first step in site selection. If a full emission inventory is not possible, then surrogate statistics such as population distribution and motor vehicle usage may prove useful. Rapid inventory techniques may be a useful means to produce initial emissions inventories (WHO, 1993; GAP Forum, 2008) using a user-friendly computer programme.

Meteorology and Topography. Prevailing meteorological conditions and topographic features will strongly influence the dispersion of air pollutants or - in the case of secondary pollutants - affect their production in the atmosphere. If used in conjunction with emission data, suitable dispersion models may be used to provide an initial assessment of likely pollutant concentrations and identify possible 'hot-spots'. Subsequent pollution measurements can also be used to test the models on which predictions are based, providing a basis for prediction in areas where monitoring is not possible.

Existing Air Quality. Monitoring may already have been undertaken in target cities. If not, special screening surveys may be designed to provide area-wise or local information on pollution problems. These often involve passive samplers and/or mobile monitoring laboratories.

Model Simulations. If available, results of model simulations can be used to predict pollutant dispersion or deposition patterns, and thus help in site selection.

Other Inputs. These may include demographic, health, population and land use information. This sort of information will serve to identify likely effects, and in particular health impacts resulting from population exposure to priority air pollutants.

The site selection process in any city must take into consideration the distribution of priority gaseous pollutants within urban environments. However, there are gaps in our knowledge of this for some pollutants such as ozone. It may not be possible to optimise measurements for all air quality parameters at one location within a city.

The answer of where to monitor involves the decision on the minimum number of monitoring sites required in the AAQM programme. It is followed by in-situ decisions on various aspects,

which may be specific to each site, viz. sampling probe height, wind flow rate, surrounding obstructions, time gap between sampling and analysis for passive and manual/semi-automated active monitoring devices. The number of monitoring sites in urban areas may be influenced by:

- the number of stationary sources with fuel combustion (PM, SO₂);
- the size and composition of the vehicle fleet;
- the irregularity of the terrain.

The AAQM sizing process involves an effective compromise among

- objective priorities;
- resource constraints;
- emission source configuration of a given area;
- atmospheric chemistry and/or diffusivity characteristics.

Because of the interdependence of these factors, the optimal number of AAQM programme sites can be chosen first by clearly defining the objectives, and then prioritizing the remaining factors.

After deciding on the optimal number of sampling sites, the AAQM sites can be spatially distributed

- in a suitably spaced rectangular grid pattern;
- in a circular grid pattern; or by
- flexible site selection representing the distribution of important receptors.

Figure 2.1 gives an example of the relative variation of the grid size for different land use categories.

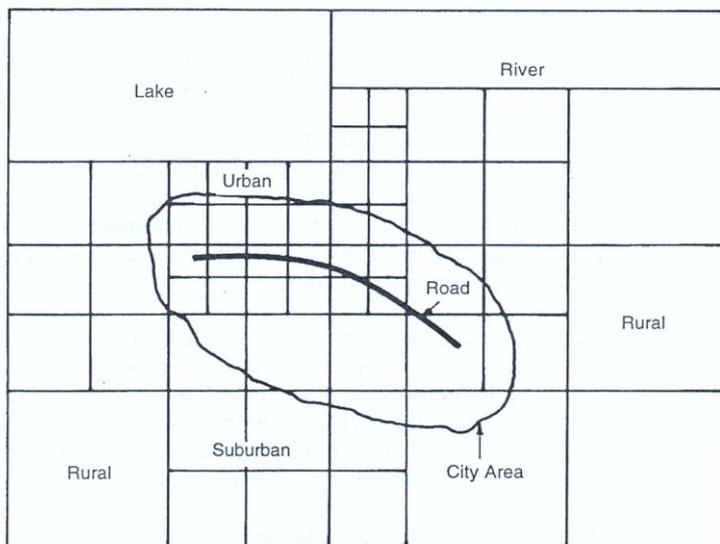


Figure 2.1: A study area divided into grid squares according to land use

In general, depending on the spatial distribution of sources, an urban area will have more spatial variation in pollutant concentrations than a suburban/rural area. Therefore, the urban area may need smaller grid sizes than suburban/rural areas. Furthermore, the grid should reflect prevailing exposure risks. A possible approach is to locate the monitoring devices

within distances which correspond to an expected concentration level change exceeding 20 per cent, calculated either from dispersion models (whenever minimum required meteorological and emission data are available) or from screening studies. Where the objectives are to evaluate possible health impacts in the population measurements should be undertaken in a number of different micro-environments. The sites should reflect the population distributions and one site should be located in a “hot spot area and another one in a control area.

Other site-specific considerations include the

- sample height;
- ensuring of free air flow to the sample site;
- bias due to nearby sources;
- accessibility to the monitoring site;
- availability of utilities (e.g. power);
- protection against vandalism.

In general, the sample height should be between 2 m and 15 m. For monitoring particulate matter (PM), SO₂, O₃, and PAH the distance of the sampling site from obstacles such as a building must be at least twice the height of the obstacle and unrestricted airflow must exist 270° around the sampler. In addition, monitoring must not be influenced by any nearby industrial or combustion activity. For kerbside monitoring of PM, NO₂ and CO the distance of monitoring sites from the edge of the traffic lanes must be at least 2 m and have unrestricted air flow of at least 180°.

2.5 When to monitor

The next important decision relates to the duration of each sampling period and the interval between two consecutive measurements. This decision may in turn help in choosing the monitoring system, i.e. passive or active monitoring equipment and the desired level of automation.

In general, sampling duration must be chosen in such a way that the defined monitoring objectives are met. Short-term sampling durations (≤ 1 hour) are necessary to record peak concentration levels and to determine the time and duration of their occurrence in studies of episodic events or for protection of sensitive receptors against very high concentration exposure. For example, a 1-hour sample period is adequate to study transport-related concentration peaks that have a 24-hour cycle.

To validate dispersion model simulations a maximum sampling duration of approximately 10 minutes or less is required since fluctuations are governed by meteorological factors, which are random in nature and can be of 1 to 5 minutes duration.

If the AAQM objective is to delineate management strategies, the air pollution problem in an area of concern has to be determined. Long-term sampling durations (≈ 1 year) are necessary for that purpose and allow characterize the cyclic nature of pollutant concentrations in an adequate way.

If the AAQM objective is to test compliance with AQS or AQG the sampling time and sampling frequency must reflect the averaging time associated to the AQS or AQG and the number of times the AQS or AQG is permitted to be exceeded in a given area.

In order to define concentration variances and confidence intervals for a desired averaging period and area the minimum required number of observations is determined by statistical needs. The criteria presented in Table 2.2 can serve as useful guidelines for the minimum required number of measurements at a site.

Table 2.2: Minimum required number of measurements at a site

Study period/time interval	Minimum number of observations
1-hour average	45 consecutive observations of 1-minute duration
8-hour average	6 consecutive hourly observations
24-hour average	18 consecutive hourly observations
Month	21 daily observations
Year	9 monthly averages (no data of two consecutive months should be missing)

If a site represents the most polluted area for gaseous pollutants and/or SPM (TSP, PM10, PM2.5), then the ambient air should be sampled at a frequency greater than the minimum requirements. For moderately polluted areas, intermittent random sampling or twice a week monitoring shall be adequate.

3. Air quality monitoring approaches

3.1 Available technologies

Air monitoring methodologies can be usefully divided into four common generic types: passive samplers, active samplers, automatic on-line analysers and remote sensors; and a fifth less common type - bioindicators. In contrast to automatic analysers and remote sensors, for which air analysis is performed automatically passive and active samples must be analyzed in a laboratory. Air sampling equipment usually consists of small pumps, filters, timers, batteries, and bottles of chemical solutions. Standard laboratory equipment includes as test tubes, beakers, balances, scales, and sometimes complex electronic instruments to find out whether samples of air contain hazardous substances or gases and how much of it is in the air sample. For low concentration monitoring precision methods such as atomic absorption spectrophotometry and gas chromatography are needed. The laboratory has to keep up with developments in equipment and methods used to control air pollution. In consequence if a laboratory does not exist the costs of its installation may be of a similar magnitude as the costs of automatic analyzers and remote sensors.

Passive Samplers for Gaseous Species. These devices, usually disc or tube-shaped, collect a target pollutant by absorption to a selected chemical substrate. After exposure for a suitable sampling period - typically from a few days to a month - the sampler is returned to the laboratory, and the pollutant is desorbed and quantitatively analysed. The main advantage of passive sampling is its simplicity and initial low cost - typically a few dollars (US) per sampler. As a result, many units can be deployed, providing useful information on pollutant spatial distributions. However the time resolution of this technique is limited, as it can only provide information on integrated average pollutant concentrations. Techniques exist for many priority urban pollutants: species for which passive samplers are available include NO₂, SO₂, NH₃, VOC's and ozone.

A special kind of passive samplers are diffusive samplers. A diffusive sampler is a device which is capable of taking samples of gas or vapour pollutants from the atmosphere, at a rate controlled by a physical process such as molecular diffusion through a static air layer, or penetration through a membrane, but which does not involve the active movement of air through the sampler (Berlin et al. 1987).

The definition also implies that, in general, diffusive sampling is not practicable for dusts or particulate matter. The uptake rate of the gas should be exclusively controlled by molecular diffusion and should not involve active movement of air. In consequence, the physical dimensions of the sampling device are the main factor governing the diffusive sampling rate. Diffusive samplers can be divided into the following types (Figure 3.1, 3.2):

- Tube type, used with or without a membrane at the open end or a windshield;
- Badge type, where the open end is protected by a membrane filter or other wind screen;
- Radial type, where the adsorbing substrate is contained in a coaxial cylindrical cartridge.

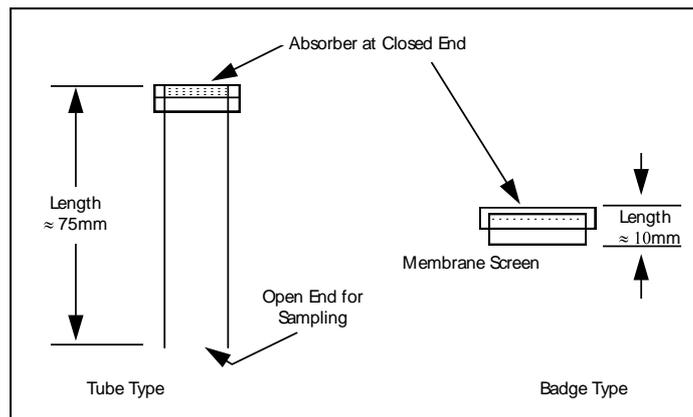


Figure 3.1: Tube and badge type diffusive samplers

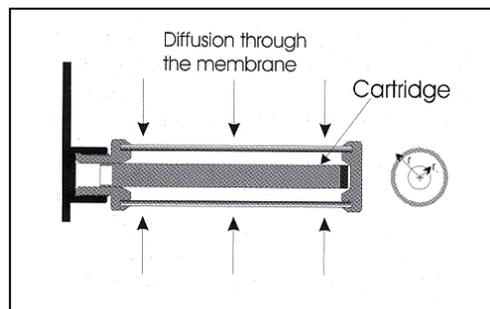


Figure 3.2: Radial diffusive sampler (Radiello)

The Radiello diffusive sampler provides the ability to conduct high-resolution concentration measurements of O₃, NO₂, SO₂, volatile organic compounds (VOC's), hydrogen fluoride (HF), hydrogen chloride (HCl), benzene-toluene-xylenes (BTX), and aldehydes.

General and specific requirements for diffusive samplers and guides to selection, use and maintenance can be extracted from the European Norm EN 13528, part 1 to part 3.

Active Samplers. Unlike passive samplers, these devices require electric power to pump sampled air through a chemical or physical collection medium. The extra volume of sampled air increases sensitivity, so that daily average measurements can be obtained. The most widely used active samplers are acidimetric bubblers for SO₂, the OECD filter soiling method for SPM (the two are often used in conjunction) and the USEPA gravimetric high-volume method for total or respirable particles. Figure 3.3 presents a general set-up for active sampling using sorbent tubes.

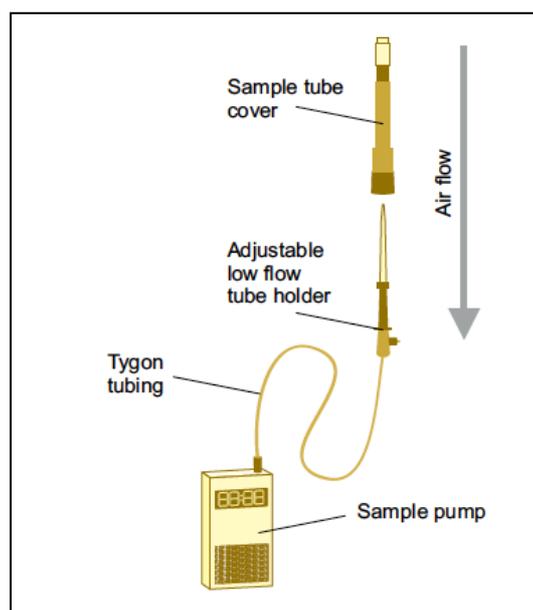


Figure 3.3: A schematic diagram of a set-up for active sampling using sorbent tubes

Active sampling techniques are available for most common gaseous pollutants - two well-known examples include the Saltzman method for NO_2 and the NBKI method for O_3 . However, these have for the most part been superseded by automatic analysers. Filter packs and denuder systems may be of use in analysing acid gases or aerosols; the latter technique, in particular, is at present the method of choice for acid air investigations.

Although somewhat more complex and expensive than passive samplers (unit costs ~\$2-4K), active samplers are relatively simple to operate and have proved highly reliable. An extensive baseline of measurements from active samplers is available for much of the world, and it is important that measurement continuity with this database is maintained so that long-term trends can be deduced.

Automatic Analysers. Despite the considerable advantages of air pollution samplers, not least in terms of ease of use, low cost and robustness, there are some monitoring applications, which necessitate the fine time response - of hours or less - provided by automatic analysers. These instruments use some physical or chemical property of the gas that can be continuously detected, usually by optoelectronic methods. Sampled air enters a reaction chamber where either an optical property of the gas can be measured directly or a chemical reaction occurs, producing chemiluminescent or fluorescent light. A light detector produces an electrical signal that is proportional to the concentration of the pollutant being measured. Portable, even hand-held, automatic analysers have become available for some pollutants. These are usually based on laser or electrochemical detection methods. However, the stability, specificity and limited sensitivity of such devices still limit their wider application.

The advanced capabilities of automatic analysers are obtained at the expense of increased capital, running and support costs: these instruments also tend to be more susceptible to technical problems than samplers, and require skilled manpower for routine operation. More sophisticated quality assurance methods may also be required for automatic analysers. Continuous analysers also produce large quantities of data, which usually necessitate telemetry systems for data acquisition and computers for subsequent processing and analysis. Well-proven continuous analysis techniques are available for the priority urban pollutants. However, it should be recognised that the relatively high cost (typically over \$10,000 per

pollutant) and operational complexity of these devices may render them unsuitable for use in some places. Their use may be inadvisable when the necessary support infrastructure and trained manpower are not available. It is common for state-of-the-art networks using automatic analysers to continue to coexist with active and passive sampler type surveys. In practice, these measurements can often be regarded as complementary activities. Automatic measurements are not necessarily intrinsically superior, and the mistake should be avoided of ceasing all sampler-based activities when automatic analysers are first deployed.

Remote Sensors. Automatic analysers provide measurements of a single pollutant at one point in space. Remote sensors, however, can provide integrated multi-component measurements along a specified path (normally > 100 m) in the atmosphere; more complex systems can even provide range-resolved measurements along the path. Particle monitoring may be assessed by the Lidar Atmospheric Profile Sensor (LAPS). Gaseous monitoring may be improved by the use of various instruments such as LIDAR, DIAL, DOAS, FTIR, OPUV and TILDAS. Mobile systems can also provide a detailed 3-D (with DIAL-techniques) map of pollutant concentrations within an area, albeit over a limited period of time. Remote sensors have unique capabilities in certain specialised applications, and can be particularly useful in near-source investigations and for vertical measurements in the atmosphere (e.g. tropospheric- and stratospheric ozone distribution).

However, at their present level of commercial development, these devices are often very expensive (>\$100,000) and extremely complex. There may also be difficulties with data validation, quality assurance and calibration. Skilled effort and careful quality control are required in order to successfully operate these systems and produce reliable data. The main advantages and disadvantages of the different generic air monitoring techniques are summarised in Table 3.1.

Table 3.1: The major instrumented air monitoring techniques

Method	Advantages	Disadvantages	Capital Cost
<p><i>Passive Samplers</i></p> 	<ul style="list-style-type: none"> • Very low cost • Very simple • No dependence on mains electricity • Can be deployed in very large numbers • Useful for screening and mapping 	<ul style="list-style-type: none"> • Unproven for some pollutants • In general, only provide monthly and weekly averages. • Labour-intensive deployment/analysis • Slow data throughput 	<p>\$10-50 per sample</p>
<p><i>Active Samplers</i></p> 	<ul style="list-style-type: none"> • Low cost • Easy to operate • Reliable operation/performance • Historical dataset 	<ul style="list-style-type: none"> • Provide daily averages • Labour-intensive sample collection and analysis • Laboratory analysis required 	<p>~ \$ 2000-20,000 per unit</p>
<p><i>Automatic Analysers</i></p> 	<ul style="list-style-type: none"> • Proven • High performance • Hourly data • On-line information 	<ul style="list-style-type: none"> • Complex • Expensive • High skill requirement • High recurrent costs 	<p>~ \$ 10000-25,000 per analyser</p>
<p><i>Remote sensors</i></p> 	<ul style="list-style-type: none"> • Provide path or range-resolved data • Useful near sources • Multi-component measurements 	<ul style="list-style-type: none"> • Very complex and expensive • Difficult to support, operate, calibrate and validate • Not readily comparable with point data • Atmospheric visibility and interferences 	<p>~ \$ 100k -300k per sensor, or more</p>

3.2 Selecting the right equipment

The data quality objectives for any monitoring system are the ultimate tool for selecting the technology. Practical considerations are also vital. These include, for example, local economic constraints, and the availability of skilled manpower. There tends to be a clear trade-off between instrument performance, cost, complexity, reliability and ease of use.

The simplest – and cheapest- method that meets the specified monitoring objectives should be selected. Inappropriate, too complex or failure-prone equipment can severely disrupt overall

network performance limiting the usefulness of the data gathered. Automatic analysers will be required if short-term concentration peaks - or resulting acute health, amenity or ecosystem effects - are to be investigated, but active or passive samplers will often be adequate if only long-term baseline levels or trends are of importance.

In fact, many baseline monitoring, spatial screening and site selection functions can be perfectly well served by active or passive sampling methods. Automatic analysers have significant cost and operational penalties, and should normally only be considered for long-term measurements (typically 5-10 years) and/or when the data quality objectives require them, e.g. for time-resolved measurements.

Remote sensors can provide integrated multi-component measurements along a specified path, but these devices remain- for the most part- complex and expensive; as such, they will usually only be considered for special applications. Similarly, although biomonitoring techniques can on occasion provide a cheap and flexible way of identifying the presence of effective levels of pollution and /or areas where more detailed measurement is desirable, they have not yet been developed to the point where they can be applied in standard monitoring programmes.

3.3 What should I measure and how should I go about it?

The last section introduced the four most widely used generic air quality monitoring approaches – passive and active samplers, automatic analyzers and remote sensors. This section introduces to specific techniques applicable for particulate matter and gaseous air pollutant concentrations. Different indicators are to be observed in monitoring for human health studies, for crop impact studies, and for ecosystem impact studies.

Monitoring for human health studies. The pollutants of concern for most human health studies are PM, O₃, NO₂, and SO₂.

Particulate matter. PM represents a complex mixture of organic and inorganic particle substances. Multiple indicators (TSP, black smoke, PM₁₀ and PM_{2.5}) are used to describe PM because of the importance of particle size in determining human exposure. Indicators like PM₁₀ and PM_{2.5} have both physiological and sampling connotations. Other indicators refer to the site of deposition in the respiratory tract, such as inhalable particles that are deposited within the upper airways and thoracic particles that deposit within the lower respiratory tract. The International Organization for Standardization (ISO) and the European Committee for Standardization (Comité Européen de Normalisation, CEN) have defined the various types of particle indicators (ISO 7708:1995; EN 1991: 481; CEN 12341: 1998).

PM₁₀ denotes particles that pass through a size-selective inlet with a 50% efficiency cut-off at 10 µm and an upper cut-off of 30 µm. PM₁₀ roughly corresponds to the thoracic particles. PM_{2.5} denotes particles that pass through a size-selective inlet with a 50% efficiency cut-off at 2.5 µm and an upper cut-off of 7 µm. PM_{2.5} corresponds to the respirable particles that can penetrate the bronchioli.

Passive monitors. Passive particle samplers can measure particle deposition, which can be transformed into particle mass concentrations only with the help of a deposition velocity according to the formula:

$$\text{Concentration } [\mu\text{g}/\text{m}^3] = \text{deposition } [\mu\text{g}/(\text{m}^2 \cdot \text{s})] / \text{deposition velocity } [\text{m}/\text{s}]$$

Deposition velocities are not usually specifically known for particles of a certain size distribution. Passive samplers are, therefore, not normally used for quantitative measurements of ambient particle concentrations.

An example of a passive monitor is the dust fall jar, which has been extensively used in some

European countries. The dust fall jar is made of an ordinary Perspex glass or plastic, with inner diameter of about 9 cm and a collection area of approximately 62 cm². The jar is placed in a wire mesh and set onto an iron bar to avoid contamination from birds and ground level influences (Figure 3.1). The dust collection period may vary from 15 to 30 days and the collected dust is reported in terms of g/(m² • d). Air suspended dust with a size range above 20 µm and having a significant sedimentation rate is expected to deposit in the jar.

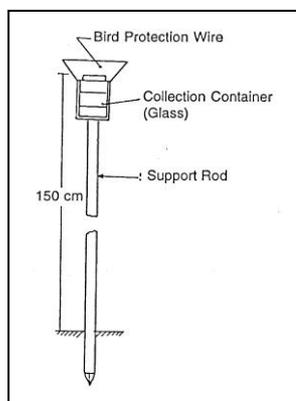


Figure 3.2: Measurement of dust deposition by the dust fall jar

Active monitors. Several types of samplers with various technical characteristics and in various price ranges can be used for PM monitoring. These samplers collect PM on a filter high-volume (~100 m³/hour) or low-volume (~1 m³/hour) pumped sample flow. The weight of PM deposited on the filter is used to estimate a 24-hour average mass concentration. Correct filter handling is fundamental to obtaining valid data. The filters must be conditioned in a temperature- and humidity-controlled environment, typically at 20°C and 50% relative humidity, for at least 24 hours before and after exposure. The filters must be accurately weighted using a suitable microbalance calibrated through an accredited method. A target accuracy figure of < 10 µg/m³ and precision of < 5 µg/m³ (for daily average concentrations < 100 µg/m³) are given for PM₁₀ measurements by CEN EN 12341 (1998) and analogously for PM_{2.5} (CEN 14907 (2005)). Several commercially available high- and medium-volume samplers have been shown to be equivalent to a reference wide ranging collector (WRAC) (CEN EN, 12341 (1998)).

A low-volume sampler (Harvard impactor) has been widely used in epidemiological and exposure assessment studies and performs well according to CEN 12341 requirements. The impactor is designed to sample particles of either PM₁₀ or PM_{2.5} at an efficiency at a flow rate of

10 litres/minute (larger particles less efficiently, smaller particle more efficiently) on a filter, which is weighed before and after sampling. The Harvard impactor is a low cost sampler of PM₁₀ and PM_{2.5} that is easy to operate and maintain (Chow, 1995).

The MiniVol Portable Air Sampler samples ambient air at 5 litres/minute for PM (TSP, PM₁₀, PM_{2.5}) and/ or non-reactive gases (CO, NO_x) simultaneously. The MiniVol provides results that approximate reference method data. Particle size separation is achieved through impaction. The PM is collected on 47 mm filters, which must be weighed pre- and post-exposure to determine particle concentrations (PO 1996-2007).

Automatic analysers. Instruments are commercially available using the following techniques:

- beta-ray absorption analysers;
- Tapered Element Oscillating Microbalance (TEOM);

- light scattering systems.

Automatic analysers of particle mass yield real-time data and do not require capture of the analysed particles for subsequent analysis. However, a shortcoming of some of these methods is that they do not directly measure particle mass, but recalculate its value based on another measured property. For example, optical counters count particles crossing the sensing area of the instrument, which is then related to particle mass; while oscillating microbalances measure changes in the oscillating frequency of a crystal or filter on which particles are sampled, and translate the change of the frequency into the mass collected. Without previous calibration of the instrument for the specific measured aerosol, the quantity measured must be regarded as an approximation. Therefore measurements from different instruments that do not measure particle mass directly are not always equivalent or comparable. An example for this is the correction formula for the PM_{2.5} concentration measured by a light scattering system – the DustTrak – and the TEOM.

The DustTRAK™ Aerosol Monitor is a portable, battery-operated laser photometer with real-time mass concentration readout and data logging capability. The monitor provides exposure assessment by measuring particle concentrations corresponding to respirable size (PM_{4.0}), PM₁₀, PM_{2.5} or PM_{1.0} size fractions (TSI, 2007). The dustTrak is originally calibrated with Arizona dust.

The relationship for urban PM₁₀ between the dustTrak and the TEOM is

$$PM_{2.5,TEOM} = 0.394 PM_{2.5,DustTrak} + 4.450,$$

which shows that the dustTrak substantially overestimates PM concentrations (*Morawska et al., 2003*).

Ozone.

Passive monitors. Diffusive O₃ samplers can be used for indicative measurements in the process of designing an AAQM network, area screening or elucidating spatial patterns of exposure.

A variety of techniques are available (UNEP/WHO, 1994; Schwela, 2003), none of them, however, has been accepted as a standard technique up to now. The most common include:

- 1,2-di-(4-pyridyl) ethylene absorbent spectrophotometry (Monn and Hangartner, 1990; Cox, 2003; Plaisance *et al.*, 2007);
- potassium-iodide (KI) spectrophotometry (Machado *et al.*, 1999);
- sodium nitrite/Potassium carbonate/ glycerol ion chromatography (Koutrakis et al., 1993; Galán Madruga *et al.*, 2001);
- indigo carmine-reflectance (WHO, 2000a).

Diffusive O₃ badge samplers and radiello samplers were validated against automatic analyser concentration data (Sjöberg et al., 2001; Delgado-Saborit, 2004; Plaisance et al., 2007).

Automatic analysers. Continuous measurement is preferred for the assessment of health effects using exposure-response relationships and compliance with air quality standards or WHO guideline values.

In general, automatic methods for monitoring O₃ employ UV absorption, a robust, well-developed and commonly used technique, of reference grade technology (ASTM D 5156-02 (ASTM, 2002); EC, 1992). UV absorption monitors are bench top instruments, and therefore are more expensive than the techniques discussed below. Ambient O₃ concentrations are calculated from the absorption of UV light at 254 nm wavelength. The sample passes through

a detection cell of known length (L). An ozone-removing scrubber is used to provide a zero reference light intensity, (I_0). The analyzer alternately measures the absorption of air in the cell with no O_3 present and with the sample, I_s . The ambient O_3 concentration, c , may be simply calculated using the Beer-Lambert equation:

$$I_s = I_0 e^{-aLc}$$

where, a , is the relevant absorption coefficient at 254 nm adjusted for temperature and atmospheric pressure. The result is:

$$c = (1/aL) \cdot \ln(I_0/I_s)$$

Given appropriate attention to sample system design, calibration and equipment support, a typical overall measurement accuracy of ± 11 per cent and precision of $\pm 4 \mu\text{g}/\text{m}^3$ should be readily achievable in well-run automatic networks.

Other methods such as chemiluminescence are less commonly used. Electrochemical and dry calorimetric methods, which are more affordable and portable, may, however, not have the desired level of sensitivity and accuracy (Knake et al., 2005; Felix & Cardoso, 2006). In general, the equipment cost for the calibration of O_3 monitors is high and requires an O_3 source and a reference instrument.

Nitrogen dioxide. NO_2 is most commonly formed in the atmosphere from nitrogen oxide (NO) emitted from combustion processes including outdoor (motor vehicles, aircraft, industry, etc) and indoor combustion sources (non-vented combustion appliances such as gas stoves, kerosene heaters and gas fired water heaters). The process of converting NO to NO_2 is very fast. NO and NO_2 are the main components of the collective term NO_x .

Passive, active and automatic analysers are available for NO_2 measurements; however for compliance against standards active samplers or automatic analysers must be used. Passive and active samplers are useful for investigations of spatial variation in NO_2 concentrations. In addition, passive samplers are well suited for personal exposure assessment.

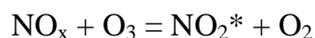
Passive samplers. Passive diffusion tubes have been widely used for monitoring of ambient NO_2 concentrations providing an integrated, average concentration for the pollutant over exposure periods of several hours to several weeks. This method is particularly well suited to baseline and screening studies for the assessment of spatial distribution of NO_2 concentrations in the urban environment. However, there are no national (or international) standards governing the application of diffusion tubes for ambient air quality monitoring nor standard operating procedures for laboratory preparation and analysis of diffusion tubes. Nevertheless there have been protocols published for sampler preparation and analysis by photospectrometry (Palmer *et al.*, 1976; Atkins *et al.*, 1986); these have been informally accepted as standard procedures for NO_2 diffusion tube preparation and analysis.

The most widely used techniques are variants on the Palmer-type sampler, which employ a tube sampler, using triethanolamine (TEA) as an absorbent. Sample analysis, after thermal desorption, is conducted by spectrophotometry or ion chromatography. Comparisons of NO_2 diffusion tube measurements with co-located chemiluminescent NO_x analysers generally show good agreement. Over the range of concentrations typically found in urban areas ($20\text{--}80 \mu\text{g}/\text{m}^3$), it was found that, on average, NO_2 diffusion tubes exposed for one month tended to overestimate ambient NO_2 by approximately 10 per cent compared with a chemiluminescent NO_x analyser. Estimates of the precision of this measurement technique have been quoted as 5-8 per cent in similar studies.

Active samplers. A review of a range of methods that are available for active sampling has been published by (UNEP/WHO, 1994; Schwela, 2003). The best known of these is the

Griess Saltzman Method, covered by ISO 6768:1998. This method is sensitive and more selective than other well established methods of chemiluminescence, and requires a relatively simple, inexpensive sampling apparatus.

Automatic analysers. The automatic chemiluminescence method is described in ISO 7996: 1985 for NO_x concentration measurements. This method is used world-wide and is defined as the reference method for compliance with EC Directive 85/203/ EEC (EC, 1985). The determination of NO_x is based on the chemiluminescent energy emitted when NO_x in the sample air stream reacts with O₃ in an evacuated chamber to form an excited energy state of NO₂. The chemiluminescent reaction is:



Light from the return of excited NO₂* to ground level NO₂ affects a photomultiplier tube and amplifier, which converts the signal into an output voltage.

The accuracy of data from automatic NO₂ analysers depends on a range of factors and has been estimated to be of the order of ± 8 per cent for NO₂ measurements in well-run automatic networks, taking account of all contributory factors. The precision of NO₂ measurements, as determined from long-term variations in baseline response of in-service analysers, is estimated to be ±6.5 µg/m³.

Sulphur dioxide.

The main source of SO₂ is the combustion of fossil fuels containing sulphur, either in power stations, domestic/commercial space heating or by motor vehicles. They are also emitted indoors from kerosene heaters and by certain consumer products. Automatic analysers need to be used if comparing against short-term standards; a variety of active samplers are suitable for comparison with daily or annual standards. Passive samplers may also be used to provide data for comparison with annual standards.

Passive samplers. As with other gaseous criteria pollutants, there are currently no national or international standards governing the application of SO₂ diffusion tubes to ambient air monitoring, nor for their laboratory preparation and analysis. However, protocols for sampler preparation and analysis by spectrophotometry and ion chromatography have been published in scientific literature. Among the most widely used passive sampling techniques (UNEP/WHO, 1994b; Schwela, 2003) are the:

- triethanolamine (TEA)/glycol/spectrophotometry method (Hangartner *et al.*, 1989);
- potassium hydroxyde (KOH)//glycerol/ spectrophotometry method (Hargreaves & Atkins, 1988);
- sodium carbonate (Na₂CO₃)/glycerine/ion chromatography method (Ferm, 1991).

Some of these techniques are also used in combination.

Active samplers. International Standard ISO 4219:1979 provides a description of the sampling equipment required for the determination of gaseous sulphur compounds in ambient air, including details of the equipment necessary to sample gaseous pollutants by absorption in a liquid bubbler. The standard also includes guidance for site selection and installation of the apparatus. This method is well established and proven, and has been used in many monitoring networks world-wide for a number of years. Consequently, there is a long history of active sampler SO₂ measurements available for trend assessment. There are several methods of SO₂ monitoring based on this principle, which differ in respect to the solutions used in the bubblers for absorption of SO₂, and the method of analysis. The most widely used methods are:

Acidimetric (total acidity) method. This method, given in ISO 4220:1983, is used to determine a gaseous acid air pollution index. Although this method measures total acidity, and is not specific to SO₂, it is adequate for general use. The simplicity of the method, and the fact that the reagents are relatively safe, make it a popular choice for routine monitoring (AEA, 1997). Taking into account all contributory factors, an accuracy of ±10 per cent has been estimated using the total acidity method, and precision of ±4 µg/m³. The use of ion chromatography instead of titration is a variant of this analytical technique.

Tetrachloromercurate (TCM) method. This is also known as the Pararosaniline or West-Gaeke method (ISO 6767:1990). This is the reference method specified in the EC Directive on SO₂ and TSP (EC, 1980). The method is sensitive in the concentration range 5-200 ppbv. The determination of SO₂ obeys Beer's law up to about 0.6 ml of SO₂ per milliliter of absorbing solution (West-Gaeke, 1956). The air is bubbled through 0.1 mol sodium tetrachloromercurate solution with formation of dichlorosulphitomercurate. SO₂ is determined by spectrophotometric measurement of the red-purple pararosaniline methylsulphonic acid when acid-bleached pararosaniline and formaldehyde are added to the scrubbing solution (West & Gaeke, 1956). However, the reagents, particularly sodium tetrachloromercurate, used are very toxic, and for this reason the method is not widely used.

Thorin method. This method is given in ISO 4221:1980. The reagents used include perchloric acid, barium perchlorate, dioxane and thorin. These are hazardous and must be handled and disposed of with care. Accordingly, this method is not commonly used worldwide.

An alternative to bubbler sampling techniques is the use of impregnated filters. Whatman No. 17 filter paper impregnated with tetrachloromercurate (II) solution is used to sample for SO₂ at levels as low as 0.05 ppbv at sampling flow rates as high as 6.5 l/min for as long as several hours. A modified West-Gaeke procedure is used for analysis. The success of this method is highly dependent upon the filter material employed (Axelrod & Hansen, 1975). The precision of the method is estimated to be 7 per cent. At levels above 1 ppbv, the accuracy of the filter method corresponds to that of the bubbler technique. The remarks on toxicity of reagents used in the modified West-Gaeke analysis applies here as well.

Automatic analysers. The measurement of SO₂ in ambient air using automatic analysers is covered by ISO 10498: 2004 (ISO, 2004). The most widely used method for automatic SO₂ measurement is ultra-violet fluorescence (UVF), which employs a convenient sampling procedure and permits high time resolution. SO₂ molecules in the sample air stream are excited to higher energy states by UV radiation at 212 nm. These energy states decay, causing an emission of secondary fluorescent radiation with an intensity proportional to the concentration of SO₂ in the sample. However, one disadvantage of this technique is the need for frequent calibration, regular maintenance and skilled workers. The sensitivity of the monitor is generally not as good as the manual method, giving uncertain results at concentrations below 1 µg S/m³. An accuracy of ±10 per cent has been estimated for SO₂ measurements in UK national automatic networks, taking account of all contributory factors. The precision of SO₂ measurements as determined from long-term variations in baseline response of in-service analysers is estimated to be ±3 µg/m³ (AEA, 1996).

Carbon monoxide

CO resulting from incomplete combustion of substances containing carbon is often present in motor vehicle emissions and tobacco smoke.

Indoor sources of CO include faulty furnaces and hot water heaters, clogged chimneys and automobile exhaust in houses with attached garages. It is a primary pollutant, and therefore its

ambient concentrations closely follow emissions. In urban areas, concentrations are highest at the kerbside and decrease rapidly with increasing distance from the road.

Passive samplers. A passive sampler has been developed for CO, utilising a zeolite absorber and a narrow filamental diffusion passage to optimise uptake, involving GasChromatography/Flame Ionisation Detector (GC/FID) analysis after thermal desorption (Lee *et al.*, 1992). This technique may be useful for screening, mapping and ‘hot-spot’ identification. Its use does not, however, appear to be widespread at the present time.

Active samplers. Grab samples may be collected for subsequent laboratory analysis using colorimetric tubes and provide a general indication of concentration levels (see: ASTM D 4599-03 (ASTM, 2003)).

Automatic analysers. The measurement of CO in ambient air is covered by international standards ISO 4224: 2000 (ISO, 2000) and ISO 8186:1989. Methods for automatic monitoring of CO include non-dispersive infrared (NDIR) spectrometry and infrared (IR) spectrometry. NDIR and IR spectrometry are the preferred baseline technology for CO monitoring, and have been routinely used for the last few decades in developed countries. CO analysis is based on the absorption of IR radiation at wavelengths of 4.5 - 4.9 μm . The monitors are either bench-top, which are more expensive and of higher performance, or hand held devices, which are cheaper and are of comparable performance with the bench-top devices. The bench-top instruments use pumps, while the hand-held miniaturized version rely on diffusion to deliver samples of the air to the transducer. Calibration of the instrument requires gas mixtures of known concentrations. Pressurized containers of calibration gases can be purchased from a variety of suppliers. Detailed methods are available in ASTM D 3162-05 (ASTM, 2005).

The accuracy of data from automatic CO analysers depends on a range of factors encompassing the entire measurement chain. These include accuracy of calibration standards, analyser stability, and sample losses in the measurement system. An accuracy of ± 8 per cent and precision of $\pm 0.5 \text{ mg/m}^3$ may be achieved using this technique in well-managed and quality assured programmes.

Monitoring for crop impact studies

Studies on the impacts of air pollution on crops serve to assess the geographical extent of risk to crops and to demonstrate the occurrence of crop impacts in selected geographical regions. Key air pollutants are O_3 , NO_2 , and SO_2 , for which WHO’s guideline values (see section 1.7) can be used as yardstick for the risk of impacts on crops.

For NO_2 and SO_2 the passive and active samplers and automated analysers presented above for human health impact studies can be used with a preference for diffusive monitors because they provide reliable results for long-term exposure.

For O_3 , the method of choice was mostly that of monitoring with automated analysers since the best indicator – AOT40 – is a complex quantity (see section 1.5). Its calculation needs the elimination of O_3 concentrations below $80 \mu\text{g/m}^3$ and limitation of the monitoring to daylight situations characterised by a solar radiation of 50 W/m^2 . As concentration and radiation vary during the six-month observation period it was thought for a long time that diffusive O_3 monitors were not applicable to solve that task.

The time-averaged data obtained from diffusive sampling does not allow one to directly measure ozone exposure in terms of AOT40. Tuovinen (2002) has, however, shown by model calculations for 8 EMEP stations that it may be possible to estimate an AOT40 value based on a measured mean concentration only, if the concentration distribution can be approximated by the Gaussian distribution and a reasonable estimate of the standard deviation is available.

Under these conditions the contribution of mean concentrations below 40 ppb to AOT40 is small as compared to the contribution at higher O₃ concentrations. Comparison with the observed AOT40 indicates that, with a few exceptions, the assumption of a Gaussian distribution results in a reasonably small (<10%) error. Thus, the assumption of a Gaussian probability density function offers a simple way to estimate AOT40 from time-integrated concentration data, such as those collected by employing the diffusive sampling technique. This interesting approach could be applied for developing countries outside Europe. More recently, Gerosa et al. (2007) have shown that concentration values obtained from diffusive sampling, together with site characteristics makes it possible to obtain AOT40 estimates for sites with no infrastructure (no electricity for real-time analyzers, not meteorological stations).

Monitoring for ecosystem impact studies

Monitoring ecosystem impacts is about measuring dry and wet deposition. Dry deposition may be broadly defined as the transport of particulate and gaseous contaminants from the atmosphere onto surfaces in the absence of precipitation (Coram, 1998).

Dry deposition is affected by the following major factors:

- a Meteorological variables (e.g., wind speed, temperature, terrain, atmospheric stability, and humidity).
- b Surface variables (e.g., surface aerodynamic roughness and structure, pH, surface charge, hydrophobicity, porosity)
- c Properties of the depositing material (e.g., chemical reactivity, solubility, diameter, surface charge, and shape).

Wet deposition is the scavenging of gaseous and particle-bound air pollutants by rain, snow, fog, or mist and their subsequent deposition on the earth's surface.

Dry deposition is responsible for 50-70% of deposition fluxes to ecosystems and wet deposition for 50-30% (Malé Manual, 2004a).

Dry and wet deposition contribute to lake acidification, eutrophication and soil contamination.

Dry deposition. Dry deposition can be either measured by surface analysis and atmospheric flux methods (direct approach) or by concentration monitoring and estimation of deposition velocities (indirect approach). Both approaches have been described in the Malé Manual (Malé Manual, 2004b). The indirect approach is currently the most feasible for routine widespread application of dry deposition monitoring. Recommended air pollutants to be monitored include TSP, PM₁₀, NO₂, and SO₂. The meteorological parameters for which data is required are: wind direction and speed, temperature, humidity, precipitation amount and solar radiation.

According to the Malé Manual, SO₂ and NO₂ are to be monitored by both active samplers and diffusive samplers as described above for human impact studies. TSP and PM₁₀ should be monitored only with a high volume sampler. The Malé Manual presents detailed advice for PM and gaseous samplers; choice of analytical instruments; instrument placement, installation and protection; monitoring protocols; treatment of samples; handling and shipping of samples; sample documentation; and sample analysis for chemical species. Although these prescription were developed for the Malé countries they are also applicable in other regions.

In order to estimate dry deposition through air pollutant concentrations and dry deposition fluxes EANET has developed a reference filter pack method (EANET, 2003). In a four-stage filter pack species collected are aerosols, HNO₃, SO₂, HCl, and NH₃. Specifications of filters

are given. By ion chromatography analyzed ions are SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} .

Wet deposition. The primary parameters to describe wet deposition are: pH, electric conductivity (EC) and concentrations of anions (SO_4^{2-} , NO_3^- , Cl^-) and cations (NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+}). Additional ions such as fluorides, bicarbonates, nitrites and organic acids may be measured if needed. Heavy metals, phosphates, aluminum and organic compounds may also be measured if necessary to characterize precipitation (Malé Manual, 2004c). The meteorological parameters for which data are required are the same as those for dry deposition.

Sampling instruments for wet deposition include (EANET, 2000)

- Automatic wet-only collectors, which open on the onset of precipitation and close on its end
- Automatic wet and dry collectors where the dry collector closes and the wet collector opens during precipitation and vice versa

The Malé Manual and other manuals provide detailed advice on the analytical instruments for monitoring pH, EC and ions (Malé Manual, 2004c; EANET, 2000; APHA, 1998; WMO, 1994). Information on monitoring protocols; collection and laboratory treatment of samples; sample handling and shipping; and suitable procedures for the analysis of rainwater major constituents are also presented. A separate chapter of the Malé Manual addresses the issue of data reporting (Malé Manual 2004d).

Recently it has been shown that under specific conditions a bulk collector can be used instead of a wet-only collector for the estimation of wet deposition (Chantara & Chunsuk, 2008). This could help reduce costs of wet deposition costs if the specific conditions are met.

4. Important issues for monitoring: quality, budget, practicality

4.1 Data quality

Before air quality data can be used to assess the situation in the area it is important to assure that the data collected are true estimates of concentrations. For each pollutant the following main questions should be answered:

- Have suitable quality assurance/quality control (QA/QC) procedures been set up
- for all stages and activities?
- Was a QA/QC plan followed rigorously?
- Has monitoring been carried out at suitable locations?
- Have suitable arrangements for data handling and storage been made and implemented?

The documentation to support the credibility of data collection and initial data quality assurance are the responsibility of the data provider. This includes the process of data collection, application of calibration factors, initial QA/QC procedures, data analysis, data “flagging”, averaging and reporting. A combination of data record notes, data quality flags and process documentation are all part of this first phase of processing. During the data collection phase, one role of the data provider is to assist in maintaining process credibility and validity of the data. The assessment makes sense only if three characteristics have been tested:

- validity
- traceability
- reproducibility.

Validity is supported by documentation that provides:

- Proof that all applicable standard scientific procedures were adhered to.
- Precise descriptions of all collected and processed numeric data including collection method; instrument type; instrument accuracy; instrument precision; data format; unit conventions; variable naming conventions; and QA/QC flags.
- Technical justification of all calculations and processes including parameter interpolations; quality assurance criteria; and scientific conclusions based upon new data processing and analysis routines built into the data management system. The last item enables inter-comparisons of new state-of-science monitoring technologies with existing technologies.
- Reference to external information upon which calculations, processes and conclusions are based.

Traceability is a documented history of all processes performed on each raw data set transmitted to the database.

Traceability is assured by maintaining tabulated, chronological listings, which summarize each step that is performed along with the method by which it is performed. It indicates the chain of steps along with the verification and quality assurance procedures implemented and

the corresponding results.

Reproducibility allows the duplication of results at any data validity level. Reproducibility requires traceability, since all processing steps performed in producing specific results must be duplicated. Reproducibility requires that all data management tools used be stored together with a chronological set of data validation records for all data sets (e.g., source codes for processing programmes must be stored and available if needed). It is of primary importance with respect to considerations of data validity, traceability, and reproducibility that data providers and the data manager make the necessary efforts to ensure that all aspects of data collection, handling, analysis, and evaluation are well documented. Documentation accompanying data are a requisite for providing a data history, which gives value to the data. To accomplish this requires that good reporting procedures be maintained and implemented at each step of data handling and processing.

A rigorously implemented QA/QC plan assures the above elements and the achievement of good quality data or at least data of known quality.

The Acid Deposition Monitoring Network in East Asia (EANET) has published a QA/QC technical document that addresses the issues of data quality objectives; role of relevant entities; QA/QC programmes; standard operating procedures (SOPs); sampling sites; measurement and analysis; data check and data quality control; data reporting; management of QA/QC activities; and training programmes (EANET, 2001).

4.2 Budget

In all decisions on what to monitor within the constraint of limited resources, AAQM programme design should be such that requirements of the monitoring objectives are met by optimizing various components of the programme.

After having decided on the monitoring objectives, the data quality objectives, the number and location of sites, the compounds to monitor considerations are to be made on the devices to monitor. As passive devices are the cheapest instruments, consideration should start with assessing their applicability for performance of the AAQM programme. Only if the monitoring objectives require more sophisticated instruments active monitors should be considered. Only if the monitoring objectives require devices with higher time resolution automatic analysers should be taken into account.

A mobile monitoring unit equipped with automatic analysers for key compounds is a nice but very expensive asset which is useless for monitoring objectives such as assessing pollutant tendencies and trends, spatial distributions, compliance of concentrations with guidelines or standards, public health and ecosystem studies. Fixed passive and active monitors will better serve these objectives.

4.3 Practicality – do's and don'ts

With little knowledge on air quality monitoring the following do's and don'ts are important:

Do's

- Always define clear and concise monitoring objectives;
- Prioritize the relevant air pollutants;
- Define achievable data quality objectives;

- Always draw up a quality QA/QC plan;
- Always use the simplest and most easy-to-use monitoring devices;
- Always calculate to total costs of an AAQM programme including equipment, human resources, need for spare parts, chemicals, and repairs.

Don'ts

- Never buy monitoring devices before having drawn up clear and concise monitoring objectives;
- Never start monitoring with complex automatic analysers as your first experience;
- Never use automatic analysers if the technical capacity of running them does not exist;
- Never allow the provision of data of unknown quality;
- Never buy a mobile monitoring system equipped with automatic analysers unless your monitoring objectives require it as the only possible solution and human resources and sufficient experience are available.

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