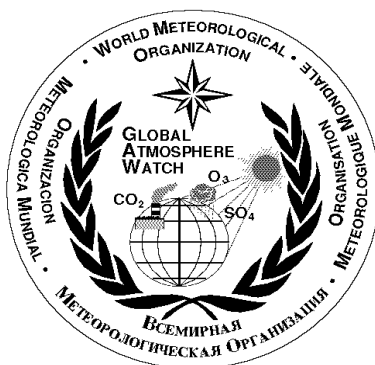


WORLD METEOROLOGICAL ORGANIZATION GLOBAL ATMOSPHERE WATCH



No. 153

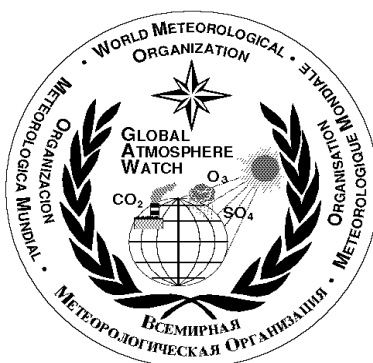
WMO/GAW

AEROSOL MEASUREMENT PROCEDURES GUIDELINES AND RECOMMENDATIONS



September 2003

WORLD METEOROLOGICAL ORGANIZATION GLOBAL ATMOSPHERE WATCH



No. 153

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WMO TD No. 1178

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PREFACE

The WMO Executive Council, through actions initiated by the Commission for Atmospheric Science (CAS) Working Group on Environmental Pollution and Atmospheric Chemistry, has placed high priority on improving the quality and spatial coverage of Global Atmosphere Watch (GAW) measurements. The WMO Scientific Advisory Group for Aerosol (SAG Aerosol) was established in 1997 to implement the aerosol measurement programme in GAW that addresses not only climate-related, but also air-quality issues. For developing countries in particular, regional aerosol pollution issues are frequently of concern. The SAG Aerosol recognizes that measurements directed at climate and regional environmental problems can frequently employ common methods.

A key role of the SAG Aerosol is drafting guidelines for measurements, proposing standards for compatible observations, quality assurance and common systems for calibration, data analysis and data archiving. This document is the product of several years of work.

The members of the WMO/GAW Scientific Advisory Group for Aerosol who contributed to it are:

Urs Baltensperger (chair)	Paul Scherrer Institute	Switzerland
Leonard Barrie	WMO Secretariat	Switzerland
Claus Fröhlich	World Radiation Centre, Davos	Switzerland
John Gras	CSIRO Division of Atmospheric Research	Australia
Horst Jäger	Karlsruhe Research Centre, Institute for Meteorology and Climate Research	Germany
S. Gerard Jennings	University College Galway	Ireland
Shao-Meng Li	Meteorological Service of Canada	Canada
John Ogren	NOAA Climate Monitoring and Diagnostics Laboratory	USA
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WMO has a history of organizing aerosol measurements as reflected in its promotion of monitoring stations globally and workshops particularly focused on aerosol optical depth such as those in 1986 (WMO/GAW Rep. #43) and 1994 (WMO/GAW Rep. #101). This report expands the guidelines on aerosol measurements from aerosol optical depth to include a comprehensive list of aerosol optical, physical and chemical measurements that are needed globally. It provides assistance to those involved in developing an integrated global aerosol measurement system for climate and environmental studies. It should be considered a working document that will be updated and revised according to new scientific and technological developments. The mention of specific manufacturers and instrument models does not imply an endorsement either by WMO or by the authors of this report.

1. INTRODUCTION

It is the goal of the Global Atmosphere Watch (GAW) programme to ensure long-term measurements in order to detect trends in global distributions of chemical constituents in air and the reasons for them [WMO, 2001a]. With respect to aerosols, the objective of GAW is to determine the spatio-temporal distribution of aerosol properties related to climate forcing and air quality on multi-decadal time scales and on regional, hemispheric and global spatial scales. This information also adds to the accuracy with which sources, transport and sinks of pollution can be determined and long-term trends for prediction of climate change can be observed. Aerosols influence the atmospheric energy budget through direct and indirect radiative effects. Direct effects include the scattering and absorption of radiation and the subsequent influence on planetary albedo and the climate system. Indirect effects involve the influence of anthropogenic aerosol on available cloud condensation nuclei (CCN). An increase in aerosol number concentration tends to increase the CCN which in turn, leads to increased cloud albedo and to changes in the Earth's radiation budget. Cloud lifetimes and precipitation frequencies can also be affected. This alters the hydrological cycle and water supply. Scientific evidence indicates that in regions with high anthropogenic aerosol concentrations, aerosol forcing is of the same magnitude, but opposite in sign to the combined effect of all greenhouse gases [IPCC, 2001]. Furthermore uncertainties are great. IPCC [2001] estimates the average direct radiative forcing, through scattering of incoming radiation, at -0.4 , -0.2 , and $+0.2 \text{ W m}^{-2}$, for sulphate, biomass and fossil fuel black carbon aerosols, respectively, and the indirect forcing, through cloud condensation nuclei effects, at 0 to -2.0 W m^{-2} for all aerosols. Long-term monitoring of chemical properties of aerosols will be crucial in determining the role that aerosols play in climate, in documenting changes in the regional air quality and in providing a scientific basis for policy decisions regarding control strategies.

In addition to climate influence, atmospheric aerosols affect many aspects of human health and the environment. Aerosol mass and its toxic chemical components are known to have links to chronic respiratory and acute cardio-vascular problems. Aerosols are also closely linked to problems of visibility reduction, acid rain, and urban smog in many locations of the world.

Aerosol impacts depend on particle size. On a mass basis, two populations of particles, with characteristically different sources, sinks, sizes and chemical compositions, generally constitute the tropospheric aerosol. The sub-micrometer fraction ("fine particles") originates from condensation sources (both high and low temperature) and from atmospheric gas-to-particle conversion processes. It is primarily removed by precipitation and dry deposition processes. In contrast, the super-micrometer fraction ("coarse particles") is produced by mechanical processes (wind driven soil erosion and seawater bubble-bursting) and is mainly removed by sedimentation, impaction and interception at the Earth's surface. It has a considerably shorter atmospheric residence time than the sub-micrometer fraction. Size-segregated measurements therefore allow the determination of the aerosol properties of each of these two populations so that their atmospheric occurrence and hence effects can be evaluated separately. It also provides data for validation of models used in scientific assessments of climate change and air quality issues.

Since the atmospheric residence time of aerosol particles is relatively short (days to weeks in the troposphere and months in the stratosphere), a large number of measuring stations are needed. The World Meteorological Organization's Global Atmospheric Watch (GAW) network consists of 22 Global stations and numerous Regional stations that cover different types of aerosols including: clean and polluted continental, marine, arctic, dust, biomass burning, and free tropospheric particles. Recently, the Scientific Advisory Group (SAG) for Aerosols of GAW recommended the development of a global aerosol network of ground-based stations. Table 1 summarizes the recommended list of comprehensive aerosol measurements to be conducted at some stations as well as a subset of core measurements to be made at a larger number of stations. Global stations are expected to measure as many of this list as possible while the GAW Regional stations and contributing partner network stations will measure the smaller set of core aerosol observations, to complete the global coverage.

The Aerosol-SAG recommends that Regional stations should measure aerosol optical depth, mass concentration and major chemical components in two size fractions, aerosol light scattering and absorption coefficients.

Table 1: *List of comprehensive aerosol measurements with a subset of core variables (identified in bold) that are recommended by the GAW Scientific Advisory Group on Aerosols for long-term measurements in the global network.*

Continuous Measurement
Multiwavelength optical depth
Mass in two size fractions
Major chemical components in two size fractions
Light absorption coefficient
Light scattering coefficient at various wavelengths
Hemispheric backscattering coefficient at various wavelengths
Aerosol number concentration
Cloud condensation nuclei at 0.5% supersaturation
 Intermittent Measurement
Aerosol size distribution
Detailed size fractionated chemical composition
Dependence on relative humidity
CCN spectra (various supersaturations)
Vertical distribution of aerosol properties

Methodologies and procedures for measuring the recommended aerosol variables are presented in the following chapters. Summaries of these procedures have been given elsewhere, along with the other components of the GAW programme [WMO, 2001b]. It should be noted at this point that suitable instrumentation is not presently available for some variables, and some calibration procedures require further international research efforts and coordination. The Institute for Tropospheric Research in Leipzig hosts the World Calibration Centre (WCCAP) for aerosol physics. To complement this important GAW facility, there is an urgent need for the establishment of a World Calibration Centre for aerosol chemistry as well as Quality Assurance /Scientific Activity Centres (QA/SACs) responsible for measurements of selected variables.

At the core of the GAW global network of Global, Regional and contributing partner stations is a willingness on the part of the participating organizations to pool their observations and make them publicly available. Public access to a comprehensive set of global aerosol observations is to be provided by the World Data Centre for Aerosols (WDCA) hosted by the Environment Institute of the Joint Research Centre, Ispra, Italy (EU). This will be done in cooperation with data centres of contributing partner networks.

GAW participants endeavour to provide precise, accurate and timely observations of the aerosol parameters listed in Table 1. In order to achieve this and as important information for the user community, the data available from the WDCA should have certain characteristics:

1. They should be traceable to the original raw observational data. This requires the maintenance of an archive of the raw data, and the history of the processes applied to that data in deriving the processed data series submitted to WDCA. Such archives are normally the responsibility of the participating organization; however the WDCA can provide limited assistance as an 'archive of last resort' where the alternative is the loss of the data.
2. They should be of known quality.

3. They should include all the information required by a user to permit the sensible use of the data. This is of particular importance in an organization like GAW where different participants may use different methods to measure individual parameters. They should include a contact point for the participant submitting the data. This aids the sensible use of the data and helps users recognize the work of the participants.

A long-term goal of the GAW aerosol data analysis and synthesis activities is to work with the GAW Global and Regional stations as well as contributing partner networks and satellite monitoring agencies to produce an integrated set of global aerosol observations. This is being done under the Integrated Global Observing Strategy (IGOS) established in 1998 by a comprehensive consortium of satellite and non-satellite observational agencies and organizations. To begin with, variables in the core subset of the variable list will be the focus of this effort.

An implementation plan for these measurements in GAW will require standard operating procedures (SOPs) for selected instrument types.

1.1 References

IPCC, *Climate Change 2001: The Scientific Basis*, J.T. Houghton, Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, X. Dai, K. Maskell, C.A. Johnson (eds), Cambridge University Press, New York, 2001.

WMO, *Strategy for the Implementation of the Global Atmosphere Watch Programme (2001-2007)*, WMO No. 142, World Meteorological Organization, Geneva, 2001a.

WMO, *Global Atmosphere Watch Measurements Guide*, WMO No. 143, World Meteorological Organization, Geneva, 2001b.

2. SAMPLING TECHNIQUES AND CONSIDERATIONS

There are many issues related to the sampling techniques that need careful consideration. The sections below deal with issues related to particle size separation and inlets, sampling media and methods, sampling setups, flow measurement and sampling frequencies.

2.1 Inlet design considerations

In this section, we provide a guideline for the common sampling considerations that apply to most aerosol analyzers and samplers at Global and Regional GAW stations. The inlet used for aerosol sampling should meet certain design guidelines so that an undisturbed aerosol is delivered to sampling or measurement instrumentation. The purpose of the inlet system is to provide a sample aerosol that is representative of ambient air, but at a controlled relative humidity, to the various aerosol analyzers and samplers in the field laboratory. Humidity control is desirable because of the strong influence of relative humidity on the size of most airborne particles. It is also necessary to exclude precipitation and to evaporate fog because of its interference with the measurements. Aerosol sampling instrumentation should generally be housed in a shelter that provides a controlled laboratory environment (temperature 15-30°C).

For instrumental measurements, sample air should be brought into the laboratory through a vertical stack with an inlet that is high enough above ground level to minimize local influences. For sites without surrounding obstructive vegetation, topography or buildings, a minimum height of 2 m above ground level is recommended. However, obstructed sites may require even higher inlets, to avoid influence by the surroundings. If possible, the sampling duct should be brought through the roof of the laboratory. If this is not possible, then a gradual bend in the inlet pipe is acceptable. Because atmospheric trace gas analyzers may have requirements incompatible with aerosol inlets, an inlet stack dedicated to aerosol sampling may be required.

An omni-directional high efficiency air inlet is required for aerosol sampling. In other words it should have a high aerosol transmission efficiency that does not vary with wind direction or wind speed. This can be achieved with a vertical air duct with a cover that excludes drizzle, rain and snow mounted on top of the inlet duct. The inlet should have a particle cut-off diameter of 10 micrometers aerodynamic diameter under ambient conditions. Sampling sites that are frequently in clouds or fog (e.g. mountain sites) should use whole air inlets to sample cloud or fog droplets as well as aerosols. This air should be dried rapidly to avoid inertial particle losses. The sample flow should be laminar in the sample tube in order to avoid additional losses of small particles by diffusion and turbulent inertial deposition. A Reynolds number of about 2000 would be ideal. For example, a Reynolds number of 2000 occurs in a pipe of diameter 10 cm and 20 cm with a flow of 150 l/min and 300 l/min at STP, respectively.

Some components of the inlet system can be built from a variety of materials, but other components require the use of specific materials. The main requirement is to use conductive and non-corrosive tubing material such as stainless-steel that are rugged, locally-available, weather- and sunlight-resistant and that do not change the size distribution or chemical composition of the aerosol particles in the sample air.

The design of an aerosol inlet can be customized by qualified engineers to fit the sampling requirements. However, these inlets must be well characterized in terms of the particle cut-off and aerosol transmission efficiencies at selected aerosol sizes spanning the size range of interest. Specifications of these custom inlets should be submitted to WMO/GAW WCCAP for review, to avoid serious sampling discrepancies between stations in the GAW network. Alternatively, commercially available inlets, whose particle cut-off and transmission efficiencies have been well characterized can be used for this purpose. Those wishing to establish GAW aerosol measurements are advised to seek advice from the WCCAP.

2.2 Size Cuts

Atmospheric aerosol particles have diameters between 1 nanometre (nm), a size where molecular clusters can resist thermal disruption, and about 100 μm where particle sedimentation rates of most particles are so high that they are not transported far through the atmosphere. Within this broad range, the atmospheric particle size distribution is a continuous, multi-modal function generally spanning up to ten or more decades of concentration. As noted by *Whitby* [1978] and others, one can conveniently express the size distribution of atmospheric aerosol particles in terms of superimposed, lognormal distributions. These distributions form modes in the size distribution and have chemically distinct compositions due to their different sources. The ultrafine mode extends from 1 nm to approximately 100 μm diameter. It often consists of two modes, the nucleation mode (up to about 20 nm diameter) and the Aitken mode (20-100 nm diameter, *Mäkelä et al.*, 1997).

The accumulation mode spans the size range from approximately 0.1-1.0 μm (100nm - 1000 nm) diameter. The coarse mode contains particles 1.0 μm and greater in diameter. Due to the hygroscopic nature of atmospheric aerosols, size increases with increasing relative humidity (RH) with the greatest change occurring above 50% relative humidity. Thus under ambient conditions in the atmosphere, the upper end of the accumulation mode of aerosols varies with relative humidity. Even at a fixed relative humidity, the modal transition points vary considerably, both spatially and temporarily. For example in marine air, the transition from the coarse to the accumulation mode can be as low as 0.4 μm diameter [*Clarke et al.*, 1987] while in continental air, it is typically 1 μm . Three aerosol modes are not always present. This variability presents a problem when defining sampling cut points for a global network – a point for further discussions below.

The accumulation mode is the most important mode for direct radiative forcing of climate. This arises from the coincidental overlap of the accumulation mode size range with the size range in which light scattering is most efficient. For human health, accumulation and ultrafine mode aerosols are most important. Particles in these modes can penetrate deep into the lung potentially impacting lung function in the short and long-term. Coarse mode aerosols are important for other reasons. They modulate the growth of the accumulation mode by offering a competing surface area sink for condensable matter formed during chemical transformation of gases. Furthermore in regions impacted by exceptionally high levels of coarse mode aerosols such as deserts (soil dust) and the marine boundary layer (sea salt), coarse mode aerosols dominate the total aerosol mass and sometimes even the scattering of solar radiation. In contrast, the nucleation mode contains very little of the total aerosol mass and it is ineffective in scattering. However, it can indicate the *in situ* formation of new particles associated with chemical transformation of gases to less volatile condensable matter.

Considering the complexity of the aerosol, it is recommended that GAW stations focus on chemical measurements of two size fractions: (i) the fine fraction consisting of the sum of nucleation and accumulation modes aerosols and (ii) the coarse fraction consisting of coarse mode aerosols. Because the modal transition points vary considerably, and because the overlap of efficient light scattering with the accumulation mode depends on the aerosol size distribution and composition, it is difficult to arrive at an ideal size cut point between the two fractions. Nonetheless, based on the limited data available to date, the following two sets of cut points are recommended: (i) 10 μm ambient RH and 1 μm dry air or (ii) 10 μm ambient RH and 2.5 μm ambient RH. These are consistent with the global average upper end point for the both the coarse and fine fractions.

The size cuts can be achieved using either impactor or cyclone inlets. For these inlets, a relationship needs to be established between the changes in sampling linear air velocity and the variations in the size cuts.

The choice of dry air versus ambient RH cuts in sampling is an issue deserving more discussion. Ideally, the ambient cut is preferred because it disturbs the aerosol least and prevents volatilization of semi-volatile constituents. It is, however, very difficult to ensure that RH in the sampler is maintained at ambient RH during sampling. Dry cut sampling maintains the RH at a sufficiently low range that hygroscopic growth effects are minimized. The end results may be combined with ambient RH measurements and hygroscopic growth factors (obtained in special measurement campaigns or estimated from chemical composition) to derive the ambient aerosol size. Because of the control on sampling RH, dry cut is preferred over wet cut. It should be kept in mind, however, that dry cut has its own problems too, particularly for semi-volatile components in the aerosols. The 1.0 μm dry air cut is recommended over the 2.5 μm cut at the ambient relative humidity (RH), since particles smaller than these sizes are usually strongly hygroscopic and the size segregation must not depend on RH. It is achieved by lowering the relative humidity to <40% prior to separating the particles with impactors or cyclones. Except for locations in the humid tropics, the reduction in RH can be accomplished by modest heating to a temperature that is maximum 10°C above ambient temperature and not to exceed 40°C. For very warm moist tropical air, there is as yet no agreed standard technique to dry the aerosols effectively. One possible approach is to carry out dilution of the ambient air with dry, particle-free air, coupled with modest heating, to achieve the low RH.

2.3 Integrated aerosol sampling and local contamination

Every site should take active measures to avoid local contamination. When siting considerations do not allow for this, integrated sampling should be done by turning off the pumps, or by-passing the sample air during conditions that lead to local pollution at the site. A combination of wind sector control and particle number (CN) concentration measurements is suggested as a control mechanism. A rapid rise in particle number concentration ($D_p > 15 \text{ nm}$) can also be used as an indicator of a local aerosol source. However, control of sampling with CN may not be a reliable control in regions that experience frequent new aerosol particle production events with associated very high particle concentration bursts. Under these situations, aerosol absorption measurements may offer a good alternative provided the local pollution aerosol is absorbing. The essential point is that each site must devise a sampling system that protects the filter samples from local contamination.

2.4 Time resolution for continuous measurements

The final data reporting protocols for the GAW aerosol data must be prepared in coordination with groups responsible for the other parameters measured at GAW sites. For continuously measured aerosol parameters, one-hour time resolution is appropriate with a measure of the central value (arithmetic mean) and variability (standard deviation) reported for each parameter for each hour.

2.5 Sampling system integrity

The integrity of the sample delivery system should be checked on a monthly basis by placing a filter on the main aerosol sampling inlet and recording the response of the continuous aerosol analyzers. The pressure drop across the filter should also be recorded. Changes over time in pressure drop or instrument response to filtered air indicate that leaks may have developed in the system, and that corrective action is necessary. The CN concentration (Chapter 5) is the most sensitive indicator of system integrity.

2.6 Standard Temperature and Pressure

All concentrations reported should be referenced to a standard temperature and pressure of 273.15 K and 1013 hPa, respectively.

2.7 References

- Clarke, A.D., The Pacific marine aerosol: evidence for natural acid sulphates. *J. Geophys. Res.*, 92, 4179-4190, 1987.
- IPCC, *Climate Change 2001: The Scientific Basis*, Houghton, J.T., Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, X. Dai, K. Maskell, C.A. Johnson (eds), Cambridge University Press, New York, 2001.
- Mäkelä, J.M., P. Aalto, V. Jokinen, T. Pohja, A. Nissinen, S. Palmroth, T. Markkanen, K. Seitsonen, H. Lihavainen, and M. Kulmala, Observations of ultrafine aerosol particle formation and growth in boreal forest. *Geophys. Res. Lett.* 24, 1219-1222, 1997.
- Whitby, K. T., The physical characteristics of sulfur aerosols." *Atmos. Environ.* 12, 135-159, 1978.

3. AEROSOL CHEMICAL MEASUREMENTS AT GAW STATIONS

3.1 Introduction

The primary goals of aerosol chemical measurements at GAW stations are: (i) to determine long-term trends locally and, taken collectively, in global distribution (ii) assess the impact of aerosols on regional and global climate and (iii) monitor regional air quality. In addition, long-term measurements of aerosol chemical size distribution can be used to evaluate and improve aerosol chemical transport models used in air quality forecast and climate models.

3.2 Critical Issues for a GAW Station for Aerosol Chemical Monitoring

Due to the complexity of aerosols, a successful network programme must address numerous issues in chemical measurement. Several guiding principles are recommended for chemical sampling and analysis in the GAW aerosol network:

- 1) Simplicity and ruggedness of the measurement system
 - i) Because the recommended techniques are to be implemented at GAW network stations, they should only require a low level of technical expertise as well as low levels of maintenance to enhance the success of the programme.
- 2) Use of a standardized aerosol filter medium
 - i) This will ensure uniformity and comparability among the stations. Quality assurance and quality control expertise or even resources can be shared among the stations.
- 3) Minimize hardware and training costs
 - i) The lower the capital costs are, the more likely it is that long-term measurements of quality will be obtained globally.

Thus, the type and number of analyses recommended here are, unless otherwise stated, the minimum that is considered consistent with the scientific objectives of the GAW network. If financial constraints dictate cutbacks, it is recommended that the cutbacks be achieved through a reduction in the number of samples that are analyzed rather than a reduction in the number of chemical species.

3.3 Recommended Chemical Sampling Techniques and Analysis

3.3.1 Sampling Media and Methods

For various chemical analyses, except organic carbon, and mass measurements, filtration with a Teflon filter is recommended for aerosol collection (Section 3.3.5.1). There are several reasons for this choice. These include: (i) the extensive use of this filtration medium in various existing measurement networks (ii) its commercial availability (iii) the efficiency of aerosol collection (at commonly used face velocities, >99% of particles with 5 nm diameter or greater will be trapped on Teflon filters of <1 µm pore size) (iv) chemical inertness (it absorbs minimal amounts of water vapour and reactive gases making it suitable for many types of chemical analyses as well as gravimetric and optical absorption measurements) and (v) low chemical content (this results in lower atmospheric detection limits; the exception is nitrate; current filters appear to have varying levels of blanks - a point for further discussion below). A filter diameter of 47 mm diameter is recommended as a standard size, facilitating the intercomparison of data and adaptation of common QA/QC procedures. It is the diameter commonly used in many existing monitoring networks. However, this does not prevent the use of other sizes. Indeed, different geometry of filter holders may be used as long as the size cut is maintained.

Quartz fibre filters should be used for organic carbon measurements. This is the only exception to the Teflon filter since the currently accepted analytical method for organic carbon, thermal desorption and evolution, requires such a specific filter medium. The quartz fibre filters must be fired before use, at a recommended temperature range of 350 - 400°C, to reduce the

organic carbon content of the filters. Given the evolutionary nature of the analytical technique, this recommendation should be viewed as an interim solution.

It is recommended that other types of filter media NOT be used particularly for stations starting the aerosol chemical sampling programme. For historic reasons, some of the existing stations may have used other filter medium types, such as cellulose-based filter media and continue to do so. These stations should consider switching to Teflon, but should have an overlap period of at least 2 years for the two measurements. Given the long-term objectives of the GAW programme, any changes in the monitoring record due to changes in sampling/analytical techniques must be carefully documented. A transition period of at least 2 years will allow these changes to be accounted for over different seasons. If, on the other hand, ongoing measurement programmes wish to continue sampling practices, a careful study must be conducted to determine whether the recommended GAW chemical measurements are compromised.

The filtration method has potential interferences, particularly for semivolatile chemical species. Interpretation of results must account for these interferences. For non-volatile species, such as sea salt and soil dust, the interferences are negligible, because either there is no gas phase equivalent for adsorption onto the filters, or the filters do not absorb the gases, or these components are stable and do not volatilize. For semivolatile chemical species, such as nitrate, ammonium, and some organic carbon species (e.g. light polycyclic aromatic hydrocarbons), interference may come from both the adsorption of gases on the filters and particle volatilization on filters during sampling. Adsorption depends on the type of filter material as well as environmental conditions, whereas volatilization is more dependent on environmental variables other than filter composition.

The face velocity at which air is drawn through a filter can affect both the adsorption and volatilization properties of particles and gases. For sulphate, volatilization does not occur; but under some special situations, such as a marine or coastal site where particles are expected to be alkaline, adsorption of SO₂ onto deposited particles and further conversion to sulphate may happen, leading to positive interference. In quartz fibre filter samplings for organic carbon in southern California, the positive bias (adsorption) has been found to be much larger than the negative bias (particle volatilization) [Turpin *et al.*, 1994]. In contrast, ammonium nitrate is particularly susceptible to volatilization from filters. According to Chow [1995], there is still a poor understanding of how well volatile compounds (and thus implicitly also PM) can be accurately measured by filter sampling. To assess the extent of interference problems, a denuder-filterpack combination may be used, particularly for the semi-volatile components. Other filter media may be used for specific measurement objectives.

In addition to filtration, impaction may be used in a programme covering the comprehensive list of measurements in Table 1. This has been most commonly used in studies of particle mass size distribution. In cascade impactor sampling, different collection substrates have been used to serve different purposes. For example, aluminium foils have been used for mass size distribution measurements, Teflon filters for chemical component size distribution, and polycarbonate filters for elemental/metal size distributions. In all cascade impactor sampling, wall losses and bounce-off are known problems and steps should be taken to minimize them. Commonly known techniques to prevent particle bouncing include humidifying the air stream to force aerosol deliquescence before impaction, and application of grease over the impaction surface. Similar to filter sampling, gas adsorption (positive artifact) and particle volatilization (negative artifact) may occur during cascade impactor sampling, particularly for low pressure stages.

The GAW guidelines do not rule out cascade impactors from being used on a long-term basis, it is recommended that these be conducted only on an intermittent basis (Table 1) to help characterize the long-term continuous filtration measurement. The same applies to denuder-filterpack measurement. If carried out, these measurements will create a large workload not only for laboratory chemical analysis, but also for the sampling and handling as well. Furthermore, specific QA/QC plans, separate from those for regular filter sampling, must be in place. The station

will probably also be on its own for auditing and calibration purposes because cascade impactor and/or denuder-filterpack sampling are not GAW core variable requirements. These add up to significant financial and resource requirements that few stations can sustain in the long-term.

3.3.2 Sampling Setup For Aerosol Chemical Analysis

For the routine long-term aerosol measurements at GAW stations, it is recommended that up to three sets of 47 mm diameter filters should be collected in parallel. If financial constraints are limiting, the priorities for filter sampling are (a) Teflon filters for gravimetric and ionic analyses; (b) quartz-fibre filters for carbonaceous aerosol analyses; (c) Teflon filters for elemental analyses. Each set would consist, ideally, of two filters, one for total mass below 10 μm diameter and one for the fine fraction. The separation would be achieved by running the filters behind the size-selective inlets as discussed in Section 2.2.

For simplicity, it is suggested that a differencing technique be utilized to separate the coarse fraction from the fine fraction. Specifically, one filter should be run behind the 10 μm diameter cut inlet. A parallel filter would be run behind the inlet suitable for the fine fraction (i.e. 2.5 μm diameter at ambient RH or 1.0 μm in dry air; see section 2.2 for details). While the second filter will yield the fine fraction, the difference between the two filters will then yield the coarse fraction.

3.3.3 Flow Measurements

Because the final measurement results are expressed in terms of air concentration (mass per unit air volume), an accurate air volume for each sample must be determined. In addition, there probably will be cases in future data analyses where mixing ratios, instead of air concentrations, are needed. This requires that ambient temperature and pressure are recorded for the conversion of units. The air volume should be reported for the recommended standard temperature and pressure of 273.15 K and 1013 hPa, respectively (section 2.6).

Air volume for each sample can be determined by integrating air flow rate over the sampling duration. There are different methods of determining the air flow rates. The most common method uses a calibrated in-line mass flow meter or mass flow controller. These devices measure the mass of air that passes through a sensor (usually by way of heat conductance measurements). The sensor should be well calibrated against known standards periodically. Mass flow meters and controllers are normally used for low to medium flow rates. For the recommended 47-mm Teflon filters, these devices are appropriate. Other flow rate measurement systems may be used, provided that they are calibrated for the operating conditions. For example, flow rates can also be determined by measuring the pressure drop across an orifice, coupled with temperature measurements. It is explicitly recommended that rotameters not be used for flow measurements at GAW stations.

For the recommended 47-mm Teflon filter, a flow rate of 15 to 30 L min^{-1} is suggested. For each sample, the flow rate should be recorded continuously on a central data collection system and properly archived. Although recommended for the 47-mm Teflon filters, it should be noted that the flow rate need not be the same at all GAW stations, as it depends on the particular sampling device, the sampling inlet and sensitivity of the chemical analysis methods. In particular, if other configurations of the filter sampling are set up to collect aerosols, such as dichotomous high volume samplers, the flow rates can be substantially higher (e.g., over 1000 L min^{-1}). After a period of one year, the suggested flow rate should be assessed and even adjusted for each station and varied to obtain the optimum number of successful samples and optimum sample load on the filters. In this case, flow rates may need to be controlled at the new rates.

3.3.4 Sampling Frequency

Several issues arise in connection with aerosol chemical sampling, issues that are interrelated and of practical importance, namely, sampling frequency and sample flow rate. One must consider the time resolution necessary to address the issues that the GAW network is supposed to resolve, and balance this against available flow rates and expected aerosol mass loadings on each sample. Simply put, the issue is about the detectability of the chemical species on each filter by the analytical method. Synthesizing these factors and based on known capabilities of analytical methods:

It may not be possible to analyze all daily samples for chemical concentration. If, due to financial constraints, not all samples can be analyzed, the following alternatives should be considered: (1) sample every day of the week and every other sample is archived, hence effectively reducing the sample analysis by half; or (2) sample every day of the week and only one sample every week are analyzed; or (3) take a daily sample every 6th day and analyze them. These 3 alternatives are preferred to a weekly integrated sample which is difficult to relate to meteorological transport conditions. In all cases, unanalyzed samples should be archived in separate, clean, dry, cool containers for possible later analysis in case of unusual events. To ensure the quality of the sampling and subsequent handling procedures, 5-10% of the samples should consist of field blanks.

The above are general recommendations. However, special exceptions can be made. For example, for stations where substantial diurnal cycles take place due to various factors (meteorology, chemistry, radiation, etc.), it is recommended that a sampling interval of 12 hours be used for the sampling programme, with the sample change timed appropriately. Conversely, stations in pristine locations may require 48 hours or more to collect sufficient sample volume for analysis.

Whether the sampled air volume is too small or too large should be reviewed at each site in the first year. The air flow rates and inlets may need re-adjustment. If overloading of the filters occurs due to excessively high air concentrations, the flow rate should be decreased. If underloading occurs due to very low air concentrations the sampling flow rate should be increased. A change of inlet may prove to be technically and financially challenging. Alternatively, the lab analytical protocols can be changed, such as dilution or concentration before analysis and with proper QA/QC documentation, to handle the overloading/underloading of samples, to achieve the optimal analytical sensitivity.

3.3.5 Recommended Analyses and Considerations

For each GAW aerosol station, a list of core aerosol chemical measurements is strongly recommended: (i) mass; (ii) major ionic species; (iii) dust aerosols; and (iv) carbonaceous components. The analytical techniques described below have proven to be capable of accounting for 85 to 90% of the measured mass and achieve an adequate aerosol mass closure. In addition to the chemical species above, individual stations may wish to consider additional analyses, such as tracer components. These analyses are discussed in detail below.

3.3.5.1 Mass

The mass concentration of atmospheric aerosols is clearly a fundamental parameter in the GAW measurement programme. It is recommended that this be done gravimetrically on Teflon filters. The aerosol mass concentration in air is commonly determined from the net aerosol mass on a filter at a recommended RH range, divided by the volume of air sampled [Chow, 1995; Willeke and Baron, 1993; Baron and Willeke, 2001; Lodge, 1988]. It is expressed in units of $\mu\text{g m}^{-3}$ where the volume is related to standard temperature and pressure (section 2.6). There are also continuous instruments for mass measurements as discussed in a separate section below.

While simple in appearance, there are many practical issues related to gravimetric measurements on Teflon filters (or any other collection medium). These arise from four areas, (1) the equilibration of the aerosol samples with the microenvironment of the balance, (2) the static electric charge on the filters, (3) the sensitivity of the balance, and (4) the changes in filter buoyancy due to changes in air density. Equilibrium of the sample with the microenvironment is the most critical issue. This is because most aerosol particles are hygroscopic. Thus, the water content can change substantially with changes in ambient temperature (T) and relative humidity (RH). Therefore, it is important to maintain a constant set of micro-environmental conditions for weighing the aerosol samples on filters and minimize the changes in both T and RH.

The net mass on the filter sample is determined from the weight difference of the filter before and after sampling. To maintain a constant T and RH, the weighing must be done with a balance in a T and RH-controlled environment. Prior to weighing, the filters should be equilibrated at the controlled constant T and RH for 24 hours.

For the GAW network, a constant temperature and RH of $20^{\circ}\text{C} \pm 1^{\circ}\text{C}$ and $45\% \pm 5\%$ are recommended.

While balances with $\pm 100 \text{ }\mu\text{g}$ sensitivities are adequate for weighing high-volume samples where 10s of milligrams of net mass are expected, electro-balances with sensitivities below $1 \text{ }\mu\text{g}$ are required for the recommended Teflon filter collection at the GAW stations. The same applies to samples collected using other low volume devices (air flow rate $\approx 30 \text{ L min}^{-1}$), especially if cascade impactors are used. Calibration of the balance must be carried out using standards of similar weights at the same microenvironment as the samples. The standards must be traceable to primary standards, e.g., those of the US NIST, or BMPI.

Static electric charge on filters is especially significant for filters with high dielectric constants such as Teflon. Charge can accumulate on filters during the manufacturing process as well as the sampling and handling processes. The charges can result in handling difficulties, enhanced or diminished particle collection, and weighing errors. Weighing error is magnified when the collected mass is small. Under the recommended GAW sampling protocol, the collected aerosol particle mass is expected to be in the range of 10s to 100s of μg . The sensitivity of the balance must be sufficient to accurately determine this. To remove any electric charge, the filter should be exposed to a corona discharge device or a low-level radioactive source such as Po-210 or Am-241 prior to and during weighing.

Accurate gravimetric analyses require the use of filters with low dielectric constants, high filter integrity, and inertness with respect to absorbing water vapour and other gases. Teflon filters, recommended for the GAW aerosol chemistry programme, meet these mass measurement requirements reasonably well. Although not recommended for use with the GAW programme, several other types of filters also meet the requirements reasonably well, including cellulose esters, and polycarbonate, which may still be in use in established GAW stations. On the other hand, cellulose fibre filters (e.g., Whatman 41) are not recommended for mass determination, because of the large and irreversible uptake of water vapour. Quartz or glass fibre filters may be used, but for high volume sample mass loadings only, where the potential loss of filter substrate material during handling is insignificant compared to the mass loadings.

These precautions notwithstanding, virtually all types of filters have a tendency to experience small changes in weight after they have been sent to the field and back without any sample on them. Therefore, along with the filters that are used for sampling, blank filters must be taken and handled in the same way as the real samples. The net mass (either negative or positive) on the blanks must be determined and used to correct the results of the samples. In addition, special care must be taken when the filters are weighed; these filters are expected to be re-analyzed for crustal and trace elements as further discussed below.

Semi-continuous instruments are also available and may be used for mass determination provided that their equivalence with gravimetric methods has been established. These types of instruments are further discussed in section 3.5.

3.3.5.2 *Ionic Species in Aerosols*

It is recommended for the GAW stations that chemical analyses be done for at least a minimum set of major ionic species in aerosols. This set includes sulphate, nitrate, chloride, sodium, ammonium, potassium, magnesium, and calcium. This selection of analyses is based on the fact that analytical procedures for them have become well established. More importantly, under most atmospheric conditions, this set of ions is expected to account for a major part of the aerosol mass, and the measurements here are an important step toward mass closure of the aerosols.

These analyses should be done using ion chromatography (IC) for the most cost-effective approach. If financial resources allow it at the GAW stations, IC should be implemented across the entire GAW network to ensure uniformity and comparability. The IC technique has the advantage of chemical speciation and relatively low cost per analysis, and has matured to the degree that the sensitivities for each ionic species, cost, and maintenance are all reasonably well known. If IC is set up properly, all the recommended ionic species can be analyzed in one single sample injection. For sodium, potassium, magnesium, and calcium, the analyses can be done without IC using atomic absorption spectroscopy (AAS) or inductively-coupled plasma mass spectroscopy (ICPMS). However, as the use of these alternative analytical techniques may introduce systematic differences amongst GAW stations, the equivalence of these alternative techniques with IC must be established and well documented.

For IC analysis, filter samples should be extracted in an appropriate amount of deionized water. A volume of 20 ml of deionized water is suggested for the recommended filter (47-mm Teflon) and total sample volume (approximately 30 m³). This will produce relatively high concentrations for most of the recommended ionic species, yet provide enough extract volume for all the analyses. Repeated analyses should be done on a regular basis (i.e. multiple analyses on one sample out of every five). The repeat analyses will give a good estimate of the analytical precision. Standards must be prepared to cover the concentration ranges seen in the samples. It is essential that the IC laboratory participate in whatever round robin interlaboratory comparison programme the GAW programme arranges for these measurements through its system of quality assurance facilities.

Additional ionic species may be analyzed for targeted studies of specific processes over extended period of time beyond the minimum set of ionic species. However, this will probably require additional IC runs for the same sample or the use of gradient technology. An example of such an additional species is MSA at marine sites. MSA is an indicator of marine biogenic sulfur emissions, and changes in MSA may indicate changes in the strength and/or processes of marine biogenic sources.

The following sections are more detailed descriptions of the ionic species recommended to be measured at the GAW stations.

Sulphate (SO₄²⁻) and Ammonium

Sulphate (SO₄²⁻) is the most studied chemical component of all and is ubiquitous in aerosols. Non-sea salt (NSS) sulphate, determined by correcting for sea-salt sulphate using the Na⁺/SO₄²⁻ (or Mg²⁺/SO₄²⁻) ratio in seawater and Na⁺ (or Mg²⁺) measurement results, dominates aerosol sulphate. NSS is one of the most dominant mass contributors to the fine fraction aerosol. But in the alkaline coarse sea salt or dust aerosols, significant amounts may be found resulting from uptake of SO₂. In the case of coarse sea salt aerosols, significant amounts of sea salt sulphate exist.

A second source of natural sulphate comes from mineral dust. This component may be corrected for by using the $\text{Ca}^{2+}/\text{SO}_4^{2-}$ ratio in mineral dust [Henning *et al.*, 2003].

Because sulphuric acid has a strong affinity for water molecules and can take up substantial amounts of water at high RH, sulphuric acid particles can grow rapidly as RH increases. This in turn affects the refractive index and scattering efficiency of the sulphuric acid aerosols. Any change in the molecular form of sulphate, such as titration of the acidity by alkaline materials, will change this sulphate-water equilibrium and particle growth, and hence the refractive index and scattering efficiency. Titration can occur through reaction with ammonia and alkaline materials such as sea salt. Hence, measurements of sulphate should be accompanied by measurements of ammonium as well as sea salt and mineral dust components, as discussed next.

For SO_4^{2-} , IC method has a high sensitivity and few problems. The same is true for ammonium ions. However, it should be cautioned that acidity titration by ammonia during filter handling processes is likely, and that special care must be taken in the handling processes to avoid contamination from this titration. This requires that stringent SOPs be established, for example, handling filters in an ammonia free microenvironment (such as a scrubbed glovebox), which is followed for the filter handling in both the field and the laboratories. Such procedures are a requirement for reliable ammonium measurements.

Nitrate and Ammonium

Nitric acid vapour is formed in the atmosphere from oxidation of NO/NO₂. Its reaction with alkaline components in aerosols leads to aerosol nitrate. It can also co-condense with ammonia vapour to form ammonium nitrate and form particles. However, the nitric acid and ammonia vapours should be in equilibrium with the particle ammonium nitrate. Alternatively, aerosol nitrate may be formed directly from reactions of various nitrogen oxides on alkaline particles without going through the gas phase nitric acid as the first step.

Because nitrate can form stable mixed salts with SO_4^{2-} salts, it can coexist with SO_4^{2-} in the fine fraction aerosol, especially in the accumulation mode. On the other hand, the reaction of nitric acid or nitrogen oxides with alkaline particles, mostly in the coarse fraction, will lead to coarse mode nitrate [Henning *et al.*, 2003]. In both coarse mode and the accumulation mode, nitrate can make a significant contribution to the aerosol mass.

In regions with predominantly ammonium nitrates and low levels of other anions, there are potential problems in sampling of nitrates arising from the volatilization of ammonium nitrate from the filters. In these situations, caution should be exercised in interpretation of data. Ancillary measurements using Teflon/Nylon filter pack samples with appropriate elimination of the gaseous nitric acid with a denuder are then recommended.

Sea Salt Ionic Components

Sea salt ionic components are important for aerosols, particularly in the coarse mode. Over the oceans, bubble bursting generates coarse and fine fraction sea salt aerosols. Sea salt aerosols dominate the mass of the coarse mode over the oceans and coastal areas, contributing much to light scattering in these regions. Measurements of sea salt components in aerosols are less prone to sampling errors. These components include the cations, sodium and magnesium. Chloride is also part of the sea salt components. However, because of the reaction of sea salt aerosols with acidic gases such as SO₂ and HNO₃, the chloride ion may be lost from the sea salt aerosols. Because the cations are non-volatile, they are not expected to experience the same sampling problems as nitrate/ammonium. Furthermore, the blank levels of these ions on Teflon filters are stable and low.

It is recommended that the Teflon filter samples from the GAW stations be analyzed for the cations using the IC technique. This technique performs the analysis well and has high

sensitivities for the recommended cations, yielding, in one analysis, all the cations along with ammonium. Separate anion analyses of the same sample will yield the chloride ion together with sulphate and nitrate, and the chloride results can be used to study the degree of acid-base reaction on the sea salt components. However, care must be taken to account for post sampling losses of chloride in the interpretation of results.

Alternatively, the sea salt components can be analyzed by the destructive methods AAS, ICPMS, or the non-destructive methods such as Instrumental Neutron Activation Analysis (INAA) or Proton Induced X-ray Emission (PIXE). PIXE is a non-destructive method for species that are not volatile in a vacuum, in which the sample may be preserved and analyzed again if handled properly. In all cases, the equivalence of these analytical methods with the IC technique should be established well, and the QA/QC procedures of the analytical methods must likewise be well established.

Other Ionic Components

It is worthwhile to have a little more discussion here about potassium and calcium ions. The major part of potassium in aerosols is expected to come from biomass burning, and hence its analysis in the GAW programme provides a long-term record of biomass burning. Calcium in aerosols, on other hand, is expected to come from dust in a variety of minerals. A small fraction of both ions can be expected to come with the sea salt components. It is recommended that both cations be analyzed with the IC method in the GAW programme. This does not constitute extra analyses, as both will result from the same analysis for the sea salt components sodium and magnesium ions, and hence no extra analytical effort is needed for both ions. Both ions can also be obtained using different analytical methods, such as AAS or ICPMS, but differences may arise due to different extraction procedures.

Other ionic species may be of considerable importance in assessing the sources of the main species discussed above in addition to the recommended minimum ionic analyses. The organic ions, including formate, acetate, propionate, and methane sulphonic acid (MSA), are good examples. MSA is a good indicator of the biogenic nss sulphate derived from dimethyl sulphide (DMS) and probably other biogenic sulphur compounds at oceanic sites, while in remote regions, the other organic anions may come from biomass burning sources. If the organic ion analysis is to be carried out, it is recommended that the Teflon filters be extracted in a sufficient quantity of solution that is enough for separate IC analyses.

Analysis for the organic ions, however, requires extra expertise in the IC technique, as it calls for an IC methodology (gradient method) that uses more sophisticated equipment (gradient pump) than that (isocratic pump) needed for the minimum analyses. MSA analysis is recommended for a GAW station in marine locations, while the organic anions are useful tracers for biomass burning in remote regions.

3.3.5.3 Mineral Dust

Mineral dust aerosols consist of crustal materials originating mostly from suspension of exposed soil by wind in arid and semi-arid areas such as desert and agricultural regions and to a lesser extent by automobile traffic on unpaved roads. Mineral dust aerosols are primarily in the coarse mode; those with diameters $>10\mu\text{m}$ fall out rapidly due to gravitational settling, while those with smaller sizes can be transported over long distances. There is plenty of evidence of hemispheric transport of dust, such as from central East Asia to the Arctic and across the Pacific and from the Sahara to Europe and the Caribbean. In such source regions and well downwind, dust aerosols dominate the coarse mode mass and sometimes even the fine mode. They can impact significantly the atmospheric energy budget through scattering and absorption of solar radiation.

Because of their stability, dust aerosols can be sampled relatively easily without the

problems posed by more semi-volatile aerosol components such as organics and ammonium nitrate. For GAW stations, it is recommended that a multi-elemental analysis approach should be used to determine the mineral dust component. Teflon filters should be analyzed for at least four of the major crustal elements Al, Si, Fe, Ti, Sc and the related elements Na, Mg, K, Ca. No specific analytical technique is recommended as there is a good selection available including PIXE, INAA, XRF, AAS and ICPMS. These techniques usually have high sensitivities for the crustal elements. Not all techniques can provide all the required elements, and depending on availability, a combination of two or more techniques may be necessary.

3.3.5.4 Carbonaceous Materials

Carbonaceous species are the least understood and most difficult to characterize of all aerosol chemical components. Total aerosol carbon mass (TC) can be divided into three fractions: inorganic carbonates, organic carbon (OC), and a third fraction called variously elemental carbon, black carbon, soot, or refractory carbon. Some of these terms are related to the measurement method used. When using optical methods, the light-absorbing component is commonly called black carbon, even though the optical method is not specific for carbon. On the other hand, thermal methods discriminate between elemental (i.e. refractory) carbon and organic carbon. For the purposes of this report, the term black carbon (BC) will be used throughout for optical measurements of the third fraction and elemental carbon (EC) for thermal methods.

The carbonaceous components are present in a large variety of forms and species. Over most continental areas and over some marine areas, carbonaceous aerosols are at least as important contributors to fine mode mass as sulphate, and TC is dominated by OC [Jacobson *et al.*, 2000]. The elemental carbon and carbonates are stable primary products whereas organic carbon is highly variable in terms of physical and chemical stability. The source of elemental carbon is incomplete combustion. Carbonate is found in crustal material and seawater. Organic carbon can come from primary anthropogenic and biogenic sources as well as secondary anthropogenic and biogenic sources.

It is recommended that TC, OC and EC be measured in the GAW programme, leaving out the relatively minor and difficult inorganic carbon component and the more complicated issues of organic carbon speciation. Sampling of aerosol carbonaceous materials is recommended using quartz filters, pre-fired at 350-400°C for 2 hours, and at the same sampling frequency as the Teflon filters. No particular filter size is suggested here, nor is the sampling flow rate. There are potential problems with this sampling method for organic carbon. Because many species of the organic carbon are semi-volatile, positive artifacts (the adsorption of organic gases onto the filters) and negative artifacts (volatilization of semi-volatile organic components from the aerosols) on the organic carbon can occur during sampling. The two artifacts may cancel each other to a certain degree, but measurements to date show that positive artifacts usually dominate the negative ones.

The best approach to correct for these artifacts is to use denuders, coated with materials such as XAD resin or activated charcoal, to trap the gases first, and then sample the aerosols using two quartz filters in sequence. This, however, requires expertise that does not normally exist at all GAW stations and adds complexities, such as special equipment to prepare the XAD denuders, to the operation. The recommendations here, of using quartz filters only, should be viewed as an interim solution. It is up to the station to make a decision on whether to adopt the more complicated denuder-filterpack combination for sampling.

The quartz filter can be analyzed for TC using the thermal evolution technique. The mass concentration of the total carbon is obtained by thermal oxidation of the carbon, usually at 750°C in the presence of a catalyst, to measurable carbon dioxide. Detection of the evolved carbon dioxide is done in one of two ways, either by reduction to methane in the presence of a catalyst, and flame ionization detector (FID), or by direct detection by non-dispersive infrared (NDIR) detectors.

The measurement of the TC components OC and EC is more difficult than the measurement of TC [Schmid *et al.*, 2001]. The NIOSH thermal evolution method has been altered

to achieve this goal [Chow *et al.*, 1993; Turpin *et al.*, 2000]. The distinction between the fractions is made by temperature-controlled volatilization/pyrolysis. This is followed by catalyzed oxidation to CO₂ and detection by NDIR, or in some instruments, further catalyzed reduction of the CO₂ to CH₄ and final detection by FID. There are different temperature-control programmes in use. Using a modified NIOSH method on a thermal optical transmittance (TOT) instrument, the OC is completely volatilized at below 550°C. At temperatures between 550-750°C, elemental carbon is converted to CO₂. At >750°C carbonate decomposes to form CO₂.

If the volatilization process is carried out under a non-oxidizing environment, some organic materials can be charred causing a positive bias in EC. This can be corrected for by monitoring the change of either the optical reflectance or the optical transmittance of the quartz filter during the heating. Even so, the separation is still semi-empirical because the temperature crossover point from one fraction to the other depends on many factors. Thus, performing the volatilization at different temperatures will yield different results, despite the application of the charring correction [Schauer *et al.*, 2003]. These uncertainties notwithstanding, temperature-controlled thermal evolution is the most accepted method of organic carbon/elemental carbon analysis. In particular, temperature-controlled thermal evolution techniques coupled with optical reflectance/transmittance correction for charring are recommended for the GAW programme for OC/EC measurement. In many research labs another procedure is followed. The temperature programming involves flash heating at 350°C and 700°C to achieve the OC/EC separation. No specific techniques are recommended. However, each measurement programme should keep a detailed record of methodology for future reference and reported to the WDCA as part of the metadata and QA report. In addition, GAW OC/EC measurement laboratories should participate in inter-laboratory comparisons whenever they are conducted.

All these measurements yield a value for the carbon concentration. For a mass balance, heteroatoms included in the carbonaceous compounds need to be taken into account as well. The factor to calculate the total mass of organic carbon differs for different species. It is 1.9 for water soluble organic carbon [Krivacsy *et al.*, 2001], and probably around 1.2 for water insoluble organic carbon. Water soluble organic carbon is typically 40 to 50% of the total carbon (except for urban sites, where it can be as low as 10%), and is usually higher in summer than in winter. Thus, the usual correction factor used for total OC (1.4) is on the low side (with the possible exception of urban sites). For comparison, Turpin and Lim [2001] give even higher conversion factors, with 1.6 ± 0.2 for urban aerosols and 2.1 ± 0.2 for aged (non-urban aerosols).

Black carbon derived from optical measurements

The optical method for estimating BC involves measuring the change in optical transmission of a deposit of particles on a filter (absorption) and applying a site-specific and instrument-type-specific mass absorption efficiency to derive BC. The recommended absorption method for measurement of the aerosol light absorption coefficient at GAW stations is described in detail in chapter 4.3. Two key assumptions are required to derive the black carbon mass concentration from light absorption measurements: (i) black carbon is the only species responsible for the aerosol light absorption and (ii) the sampled black carbon has the same mass absorption efficiency as the standards used in laboratory calibrations of the absorption instrument. These assumptions can be evaluated by experimentally determining the mass absorption efficiency by simultaneously making light absorption measurements and EC measurements as described above. At sites where EC concentrations are not routinely determined on quartz-fibre filters, less frequent filter collections can be used to derive site- and season-specific values of the mass absorption efficiency. Thus, for GAW measurements of BC experimentally derived values of the mass absorption efficiency at a site are essential when estimating black carbon mass concentration from light absorption measurements.

Similarly for OC determination, there is an indirect method that is commonly used. The non-destructive technique PESA (Proton Elastic Scattering Analysis) done simultaneously with PIXE is used to determine the hydrogen content of aerosols collected on Teflon filters. The

hydrogen measurements are then corrected for inorganic hydrogen using simultaneous measurements of sulphur (or sulphate) and nitrate to obtain the remaining hydrogen associated with organic carbon. This organic hydrogen is then converted to organic carbon content using an assumed H/C molar ratio (usually 1.2 ± 0.2) for the organics [Cahill *et al.*, 1989; Malm *et al.*, 1994]. Organic carbon estimates using the PESA technique often yield acceptable aerosol mass closure. The technique provides organic carbon measurements on the same filter as multi-elemental analysis is done by PIXE or XRF without the need for a second sampling of aerosols on quartz filters that is required by the thermal evolution technique. PESA and PIXE analyses are usually provided by analytical services associated with large facilities possessing tandem ion accelerators. Long-term measurements of this type should follow an accepted operating procedure and have a documented QA/QC programme. If this approach is used to make OC measurements at a GAW station, it is recommended that a periodic determination of OC using the thermal method is conducted so that results can be compared.

3.3.5.5 Trace Components

Trace components of aerosols are important as indicators of sources and processes. Some may have health effects. Tracers include both elemental and molecular forms. Due to cost considerations and the necessity to limit the number of samples, routine analyses of these species are not recommended at each GAW station. However, studies should be considered for assessment purposes on a case by case basis. For example, the gravimetric and optical absorption techniques are non-destructive and the filters for these methods could be archived for later multi-elemental analysis by PIXE/XRF/INAA for transition metals. When analyzing for elements related to dust aerosols, many of the transition metals can be also obtained for limited incremental costs. For example, in PIXE analysis, a long list of transition metals, including Ni, Cu, Zn, Fe, Pb, are obtained from the same analysis as for Al, Na, Mg, K, and Ca, all of the dust components.

The speciation of organic carbon can be used for source identification and apportionment. Some species have been successfully used as tracers for identification of major sources of the organic carbon [Hildemann *et al.*, 1994; Schauer *et al.*, 1996]. Organic compounds can originate from primary sources (natural biogenic or anthropogenic) and secondary anthropogenic sources. While much work has been done in urban atmospheres, little data are available from rural and remote locations such as the GAW stations. The amount of (primary) emitted carbonaceous biological material can be assessed by special methods [Matthias-Maser and Jaenicke, 1994]. For example plant wax bears unique carbon preference indices (CPI).

Sampling for these organic carbon species has traditionally been done with quartz or glass fibre filters, again with the potential for artifacts formation as discussed above. There are many different chemical analysis techniques for organic compounds in aerosol OC often involving some form of liquid or gas chromatography. These methods are closely coupled with the sample handling procedures. For example, a simple procedure for thermal desorption of aerosols on quartz filters has been used for analysis of polycyclic aromatic hydrocarbons (PAHs) with GC/MS systems. To obtain more species, complicated extraction procedures must be used, typically with solvent extraction, followed by separation of the extracts into fractions with different polarities. These fractions are then analyzed using different GC columns to obtain polar and non-polar compounds such as long chain alkanes and a more complete list of PAHs. The polar fraction are usually further derivatized to improve the sensitivity of the GC for the compounds, such as the long chain acids. Systematic and long-term comprehensive measurements such as these are yet to be carried out at any location and are not recommended as a GAW long-term routine measurement. However, periodic characterization studies of aerosol organic carbon speciation at suitable GAW stations are encouraged. Such studies will help identify the sources of organic carbon components. Collaboration of GAW network stations with those few laboratories having a demonstrated expertise is highly encouraged for these types of studies.

3.3.5.6 Water

Water in aerosols is rarely measured in a network programme, but it is closely related to the climatic effects of aerosols. When the hygroscopic constituents of aerosols take up water, both the aerosol mass size distribution and the refractive indices change. This directly affects the aerosol scattering and mass balance (see 4.2 for the effect of water uptake on the scattering coefficient).

The amount of water can only be measured with in-situ instrumentation. Several approaches have been recently developed. One such instrument is tandem differential mobility analyzers (TDMA) in which aerosols are dried before the first DMA and re-humidified before the second DMA. The TDMA monitors the growth of aerosols of selected sizes between the dry and humidified conditions [Weingartner *et al.*, 2002]. A similar approach monitoring changes in light scattering of aerosols with nephelometers before and after dehumidification and re-humidification has been used (section 4.2). Another approach is to estimate the water content based on the equilibrium between water vapour and aerosols. This is done using the major aerosol ionic components, the ambient RH, and known thermodynamic properties of these components [Tang *et al.*, 1978; Tang and Munkelwitz, 1994]. Systematic measurements of aerosol water content should only be done during intensive aerosol characterization studies at GAW stations and not on a long-term basis.

3.3.6 Location and Distribution of Analytical Chemistry Facilities

A global atmospheric aerosol chemistry effort will involve collaboration between GAW and contributing partner networks. In order to merge the observations, laboratories must routinely participate in a laboratory intercomparison programme coordinated through a World Calibration Centre for Aerosol Chemistry (WCCAC) and report the comparison results to the WCCAC and WDCA. Although it is desirable to minimize the number of chemical laboratories within a network, there are also advantages in distributing the chemical analyses amongst enough laboratories within the network to minimize the time between sample collection and analysis. This is particularly true for mass and major aerosol ionic constituents. Furthermore, there are advantages in national capacity building. For multi-elemental and carbon-related analyses, where large analytical facilities and a great deal of expertise are required, respectively, it is recommended that the analyses be done at as few facilities as possible.

3.4 Sample Handling Protocol

This chapter provides general guidelines for a sample handling protocol for filter based chemical aerosol measurements at GAW stations. Detailed protocols can be worked out by the national network. Filters should be loaded into filter holders (filterpacks) in a clean environment at a central facility to minimize the need for clean room facilities and associated training at each site. Contamination and filter loss are avoided by minimizing filter handling. The loaded filterpacks should then be shipped sealed to the stations. A significant number, between 5-10%, of all filters and filterpacks should be used as field blanks. Field blanks are treated exactly like a sample even to the point of mounting them in the sampling device. The only difference is that air is not drawn through them. Sampling should be avoided during episodes of local pollution (see Chapter 2.4). Presumably, the site selection process of the GAW station will have minimized the impact of local pollution; nonetheless, criteria must still be developed to minimize the effects of local pollution on the measurements and instrumentation designed to implement the criteria. Field logs for each sampled filterpack must be maintained. The logs must record all relevant information related to the particular filterpacks during sampling, including brief description of the meteorological conditions for the sampling period, and activities that may affect the sampling, and other QC flags. The exposed filterpacks should be resealed after sampling, stored in a dark location and returned to the laboratory as soon as possible to minimize the time between sampling and analysis. During shipping to the laboratory and during storage at the laboratory, samples should be kept cool to avoid volatilization and chemical changes. Field logs of critical sampling information should be copied and

sent along with the filterpacks to the laboratory. Ideally, flow rate records should also accompany the filterpacks to the laboratory. In the laboratory, such information can be used in screening for proper sampling.

Filterpacks should be unloaded in a clean environment, for example, in a filtered flow hood or glove box in which the air contains no particles, ammonia or other semi-volatile gases. The filterpacks need to be cleaned before new filters are loaded again.

3.5 Continuous Instrumentation

Over the last few years, research efforts have been made to automate and combine the tasks of aerosol sample collection and analysis, and to develop continuous or semi-continuous instrumentation [Baltensperger *et al.*, 2001]. These efforts, if successful, will reduce sample handling and the potential chances of contamination and confusion. At this time, various instruments are at different stages of development.

The TEOM (Tapered Element Oscillating Microbalance) has been widely used for aerosol mass measurements. The instrument provides continuous measurements and can produce high time resolution data. The original TEOM has a recommended temperature setting of 50°C. There is evidence that semi-volatile components of aerosols are lost from the TEOM measurements at this temperature. The most likely explanation is that semi-volatile organic compounds, nitrates, and water are lost from the aerosols during sampling. In newer TEOM models, the operating temperature has been lowered to 30°C to reduce losses of the semi-volatile components. In addition, sudden changes in ambient relative humidity may cause negative mass readings from the instrument. New modifications have been made to dry the aerosol particles before measurement to reduce the effect of ambient relative humidity [Baltensperger *et al.*, 2001].

A different type of instrument for continuous mass measurements, the β -meter, has also been commercialized. It operates on the principle of β -ray attenuation by a layer of aerosol. The β -ray source is usually ^{14}C or ^{85}Kr decay and the attenuation can be calibrated with a known mass. Sampling can be done with individual filters or filter tapes, and the β -ray that passes through the filter is continually monitored. The β -meters have the same inherent difficulties concerning volatilization as the TEOM. However, comparison with gravimetric methods usually produces reasonable agreement [Baltensperger *et al.*, 2001].

In terms of chemical components in aerosols, there are also technical developments that have implications for the GAW measurement programmes. Instruments are emerging on the scene for continuous and semi-continuous measurement of sulphate, nitrate, and organic carbon/elemental carbon in aerosols. These techniques collect aerosol particles onto impaction plates and convert sulphate and nitrate into SO_2 and nitric oxides for detection. For example, Stolzenburg and Hering [2000] recently demonstrated a system that samples aerosols by impacting them onto a metal plate, vaporizing the particles at high temperature, and converting nitrate into NO_x for detection by chemiluminescence. The comparison with denuder-filterpack measurements of nitrate is reasonable. On the other hand, efforts to carry out continuous measurements of organic carbon/elemental carbon are largely unsuccessful due to a number of technical difficulties. The most recent development in aerosol mass spectrometry involves the continuous measurement of size distribution of sulphate, nitrate, ammonium, and total organics.

It should be noted that the continuous and semi-continuous instrumentations are not a panacea to the GAW aerosol chemical measurement programme. While there are obvious advantages of deploying these types of instruments in place of the regular filterpack sampling programme, there are also many issues with using these instruments for long-term trend measurements. Firstly most instruments are still in the developmental stage and will not be available or fully tested for some time and not suited to unattended operation. Secondly, those instruments currently in use lack standards to audit or calibrate them on a regular basis. Thirdly, the costs for a comprehensive aerosol chemical composition monitoring programme using

continuous/semi-continuous instruments are expected to be higher than the regular filterpack sampling/laboratory analysis and thus limiting the spatial coverage possible. This is because most continuous/semi-continuous instruments are capable of measuring only one chemical component. Hence for a comprehensive aerosol composition determination, many types of continuous/semi-continuous instruments would be needed to replace the regular filterpack sampling/laboratory analysis approach.

If these instruments are to be used to replace the regular filterpack sampling/laboratory analysis recommended by GAW, an equivalence must be established between the two methods.

3.6 Quality assurance and quality control plans

The goal of a GAW chemical aerosol measurement is for accurate long-term records, on a decadal or multi-decadal scale. Hence it is imperative that the measurement activities be quality assured and the data quality controlled, preferably by designated personnel. Here a general description of QA/QC principles are given, intended as a basis from which the individual stations can modify or adopt as their guidelines for the long-term QA/QC plans. In addition to the field logs, it is recommended that for GAW stations undertaking the chemical measurements, a record of sample recovery rate for each network station should be maintained on a fixed schedule, such as monthly or quarterly. These records can be used as a basis for corrective actions if needed.

Compliance with the standard operating guidelines and procedures for sampling and analysis should be documented on the same schedule. For these matters, compliance criteria from the SOPs must be developed against which checks can be made. After completion of chemical analysis, QC checks must be performed on the raw data to flag questionable analyses that need repeat analyses. All analytical results must be properly combined with field data, such as air volume for each sample, to derive the final air concentration data. All such data must be recorded using well-documented formats on an electronic data system as described in chapter 9. Data that needs to be recorded include sampling data, sampling flags, calibration data, sample recovery rate survey, analytical results, lab flags, and compliance. These data must be combined with the ancillary measurement before they are recorded at the central data centre.

Analytical procedure quality control should consist of at least three steps: (1) performance check by involving the lab in inter-laboratory intercomparisons, (2) distribution of QC standards with regular samples in a routine analysis sequence, and (3) regularly scheduled repeat analysis of the same samples. Separate sets of flags must be developed for sampling/sample handling and analysis. The flags must be recorded with final results before submission to a central repository. Quality assurance includes regularly scheduled calibrations, as well as flagging of data with known problems for continuous and on-site measurements. It must be emphasized that proper standards must be used to calibrate these instruments. The raw data, along with the flags and the calibrations, must be properly archived. On a regularly scheduled basis, these data must be properly converted into final concentrations and be recorded using a predefined format for submission to a data centre. Data delivery to the GAW World Data Centre for Aerosols should be done on the same schedule as the sample recovery survey.

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4. IN-SITU MEASUREMENTS OF AEROSOL RADIATIVE PROPERTIES

4.1 Introduction

Knowledge of aerosol radiative properties is needed for evaluation of aerosol effects on climate and visibility. The fundamental quantity of interest for these applications is the aerosol cross-section for light extinction per unit volume of air, commonly called the aerosol light extinction coefficient (τ_{ep}) and reported in units of $m^2 m^{-3}$ (i.e., m^{-1}), km^{-1} , or Mm^{-1} . The light extinction coefficient is the sum of the light scattering (τ_{sp}) and light absorption (τ_{ap}) coefficients. Local visual range is related to the total light extinction coefficient (at 550 nm wavelength) by the *Koschmieder* [1924] relationship, $V = 3.9 / \tau_e$, where scattering and absorption by both particles and gases contribute to the total light extinction coefficient. Scattering by gases (τ_{sg}) is a well-known quantity that is directly proportional to air density and inversely proportional to the fourth power of wavelength, with a value of $12.3 Mm^{-1}$ at standard temperature and pressure (273.15 K, 101.325 kPa), at 550 nm wavelength. Absorption of solar radiation by gases is generally negligible compared to scattering, except in plumes containing high concentrations of NO_2 .

For radiative climate studies, information on the angular distribution of scattered light and on the relative amounts of scattering vs. absorption is required, in addition to the integral through the vertical column of the aerosol light extinction coefficient (aerosol optical depth, see Chapter 7). Combined interpretation of aerosol optical depth and surface-based measurements of aerosol light scattering and absorption coefficients requires knowledge of the vertical distribution of aerosols, which can be obtained from LIDAR measurements (see Chapter 8). Additional information on the mass scattering efficiency of major aerosol species, combined with knowledge of the dependence of aerosol radiative properties on relative humidity (RH), allows calculation of aerosol radiative effects from model predictions of spatial distributions of various aerosol species. *Ogren* [1995] and *Heintzenberg and Charlson* [1996] have presented overviews of the aerosol properties needed to determine the influence of particles on the Earth's radiative balance, and Table 4.1 gives a summary of these properties.

Table 4.1: Aerosol radiative properties needed for climate studies

??	Aerosol optical depth , defined as the integral over the vertical column of the aerosol light extinction coefficient.
τ_o	The aerosol single-scattering albedo , defined as $\tau_{sp}/(\tau_{ap}+\tau_{sp})$, describes the relative contributions of scattering and absorption to the total light extinction. Purely scattering aerosols (e.g., sulphuric acid) have values of 1, while very strong absorbers (e.g., black carbon) have values of around 0.3.
g, τ	Radiative transfer models commonly require one of two integral properties of the angular distribution of scattered light (phase function): the asymmetry factor g or the upscatter fraction τ . The asymmetry factor is the cosine-weighted average of the phase function, ranging from a value of -1 for entirely backscattered light to +1 for entirely forward-scattered light. The upscatter fraction τ gives the fraction of sunlight scattered in the upwards direction (back to space), which depends on the solar zenith angle as well as the size distribution and chemical composition of the particles. τ can be estimated from hemispheric backscatter fraction b (see chapter 4.2).
τ_{si}	The mass scattering efficiency for species i , often calculated as the slope of the linear regression line relating τ_{sp} and the mass concentration of the chemical species, is used in chemical transport models to evaluate the radiative effects of each chemical species prognosed by the model. This parameter has units of $m^2 g^{-1}$.
τ_{ai}	The mass absorption efficiency , for species i , often calculated as the slope of the linear regression line relating τ_{ap} and the mass concentration of the chemical species, is used in chemical transport models to evaluate the radiative effects of each chemical species prognosed by the model. This parameter has units of $m^2 g^{-1}$.
$f(RH)$	The functional dependence of components of the aerosol light extinction coefficient ($\tau_{ep}, \tau_{sp}, \tau_{ap}$) on relative humidity, expressed as a multiple of the value at a low reference RH (typically <40%).

All of the above parameters are needed as a function of wavelength. The Ångström exponent, α , defined by the power-law $\tau_{sp} \propto \lambda^{-\alpha}$, describes this wavelength-dependence for scattered light. The literature on aerosol optical depth uses the symbol α to denote the Ångström exponent. However, the symbol α is also used to denote the aerosol mass scattering and absorption efficiencies, necessitating the use here of a different symbol for the Ångström exponent.

Similar formulations are used to describe the wavelength dependence of aerosol optical depth and light absorption. Situations where the scattering is dominated by submicrometer particles typically have α of approximately 2 (for the 550-700 nm wavelength pair), while values close to 0 occur when the scattering is dominated by larger particles such as mineral dust. Several wavelengths, spanning the visible spectrum, are recommended for GAW measurements. It would be desirable to harmonize these wavelengths with ones used by other spectral sensors to monitor the atmospheric aerosol (from surface-based or satellite-borne remote sensors), but there is a large number of wavelengths currently in use. Thus, comparison with other instruments will often require interpolation between whichever wavelengths are used. Many of the instruments for determining aerosol light scattering and absorption coefficients have a channel at about 550 nm, which is near the middle of the visible spectrum and provides a reference wavelength for comparing different sites and for comparison with standard visibility observations. *Blanchet* [1982] showed that values of τ_{ep} , τ_o and g measured at about 700 nm wavelength can be used in radiative transfer models to represent the values of these parameters averaged over the solar spectrum. Thus, 700 nm is a good choice as a second wavelength after 550 nm for use in climate studies.

4.2 Light Scattering

Aerosol light scattering coefficient, τ_{sp} , is measured with an integrating nephelometer [see e.g., *Heintzenberg and Charlson*, 1996]. Integrating nephelometers have been operated at baseline monitoring stations since the deployment of a four-wavelength instrument at NOAA's Mauna Loa Observatory in 1974. At present, there are about a dozen sites monitoring τ_{sp} routinely around the globe, many of them part of the GAW global network. A few of these are operating single-wavelength units, but most are measuring τ_{sp} at three wavelengths. At present, there is only one multi-wavelength integrating nephelometer that is commercially available: the TSI model 3563 (TSI, Inc., St. Paul, USA). This instrument operates at wavelengths of 450, 550, and 700 nm, and has the added feature of being able to measure τ_{sp} over two angular ranges: total scattering (7-170° degrees) and hemispheric backscattering (90-170°, denoted as τ_{bsp}). While instruments do not exist for direct determination of the asymmetry parameter, g , or upscatter fraction, τ , the ratio $b = \tau_{bsp}/\tau_{sp}$ can be used to estimate either of these parameters [*Marshall et al.*, 1995; *Wiscombe and Grams*, 1976]. The high sensitivity, multiple wavelengths, and backscatter capability of the TSI 3563 makes it most suitable for monitoring aerosol light scattering properties in support of radiative climate studies. Simpler, less expensive, less sensitive, one-wavelength instruments are also commercially available. These instruments can provide useful information on aerosol light scattering coefficient at regional sites where aerosol loadings allow the use of a less sensitive instrument. The procedures described below are based on experience with operating the TSI 3563, but the general considerations apply to other nephelometers as well.

Anderson et al. [1996] reported the results of a comprehensive laboratory determination of the performance of the TSI 3563 integrating nephelometer, including characterization of its sensitivity, linearity, angular response, and wavelength response. They reported that instrument "non-idealities introduce uncertainties of less than 10% for typical accumulation mode particle sizes (i.e. volume mean diameters between 0.2 and 0.4 μm)", but the errors in τ_{sp} for particles larger than 1 μm diameter are 20-50%. *Anderson and Ogren* [1998] recommended several specific operating procedures for the TSI 3563:

1. The preferred calibration gases are air and CO₂.
2. Routine measurements of the calibration gases are desirable.
3. Supermicrometer particles should periodically be excluded from the sample stream. A cut size of 1 μ m (aerodynamic diameter at low RH) is recommended.
4. For extinction budget studies, correction factors for the effects of angular non-idealities should be applied.

Calibration is achieved by filling the instrument with a particle-free gas that has a known scattering coefficient. Most instruments use filtered, ambient air as the downscale calibration point, and CO₂ as the upscale point. Generally, calibrations with air are performed automatically every few hours (or every few minutes, in instruments without internal pressure and temperature sensors). It should be made clear that the schedule for air calibrations controls the precision of the determination of the Rayleigh scattering coefficient of air, which is subtracted from the measurements to obtain the aerosol light scattering coefficient; any error here gravely affects the detection limit of the instrument. Calibrations with other gases are performed much less frequently (every 2-12 months). Tests by NOAA/CMDL with weekly measurements on CO₂ indicate minimal calibration drift over a 7-month period, with standard deviations of the derived τ_{sg} value for CO₂ ranging from 0.7-3.5% of the mean value.

τ_{sp} shows a strong dependence on relative humidity, and interpretation of nephelometer data requires knowledge of the RH in the sample volume. This RH is generally lower than the RH at the inlet due to heating of the air by the light source. For the TSI 3563, this heating is typically 4-5°C, but it can be reduced to about 1°C by operating the instrument with the covers removed and using an external fan to increase ventilation around the lamp. Fortunately, the RH-dependence below about 50% is fairly weak, so a precise determination of RH is not required if it is kept below this level. Comparison of results from different locations is facilitated by choosing a reference humidity for operating the instrument. The inlet system used at a GAW aerosol sampling site will likely include RH-control, obviating the need for a separate RH-controller for the nephelometer. However, the recommended sampling protocol includes measurement of RH inside the nephelometer, and we recommend a value of 30-40% for the reference relative humidity.

Measurements of $f(RH)$ require a second nephelometer, directly downstream of a humidifier. *Anderson and Ogren* [1998] reported minimal particle losses in the TSI 3563 nephelometer, making it appropriate to operate the humidified nephelometer downstream of a nephelometer operated at a low, reference RH. The expense and complexity of this measurement preclude its implementation at most GAW sites, but it would be desirable to obtain these measurements at a range of sites that covers a variety of aerosol types.

Aerosol filter samples should be collected in two size fractions (see Chapter 3). One of the derived products from the GAW nephelometer sampling will be values of the mass scattering (and backscattering) efficiency for the chemical species determined from the filter samples. Accordingly, the aerosol supplied to the nephelometer should be size-segregated, with the same size cuts as used for the filter samples. This can be achieved by placing an impactor, in parallel with a ball valve, in the air stream ahead of the nephelometer. By automatically opening and closing the ball valve every few minutes, values of the total (<10 μ m diameter) and submicrometer aerosol light scattering coefficient can be determined. However, the success of this approach requires a nephelometer with internal pressure and temperature sensors to automatically compensate for changes in sample air density induced by the impactor.

Routine maintenance for integrating nephelometers is minimal. The lamp and zero air filters are the only consumables in the instrument, and are easily replaced. Insects (and even birds!) have found their way inside nephelometers, but their effects are readily detectable in the data. With time, dust accumulation on interior surfaces can result in unacceptably high background levels, necessitating disassembly and cleaning. The key to identifying the need for maintenance is to maintain daily logs of diagnostic parameters (lamp current and voltage, internal reference

brightness, power supply voltages, air calibration results), and to train the site attendants to look for gradual degradation or sudden changes in those parameters.

Some integrating nephelometers are equipped with pressure and temperature sensors to allow compensation for changes in the scattering coefficient of air due to density changes. Internal relative humidity sensors are also available. The calibration of these sensors should be checked on an annual basis.

4.3 Light Absorption

Instruments capable of high time-resolution determination of aerosol light absorption coefficient are commercially available, based on the rate of change of transmission through a fibre filter as particles are deposited on the filter. Calibration of these filter-based methods is difficult, but is required because the relationship between change in light transmission and aerosol absorption optical depth on the filter depends on many factors, including the particular filter medium and the light-scattering nature of the particles. *Heintzenberg et al.* [1997] discuss the methods used to determine τ_{ap} , and conclude "there is a clear-cut need for standardization and intercalibration of measurements of light absorption coefficient." *Bond et al.* [1999] and *Weingartner et al.* [2003] have presented successful approaches for this calibration, which require simultaneous nephelometer measurements to correct for substantial effects of light scattering by the particles on the filter. These calibrations are only available for instruments making narrow band absorption measurements therefore it is recommended that narrow band instruments should be introduced across the GAW network.

One instrument in common use is the Aethalometer (Magee Scientific, Berkeley, USA). Originally, this instrument was calibrated in terms of an equivalent mass of black carbon rather than the fundamental property that provides the instrumental response: aerosol light absorption. Interpretation of Aethalometer data in terms of black carbon requires a value for the mass absorption efficiency of the black carbon particles. When deposited on the filter, a value of $19 \text{ m}^2 \text{ g}^{-1}$ is commonly used. However, mass absorption efficiencies ranging from 5 to $20 \text{ m}^2 \text{ g}^{-1}$ have been reported for aerosols from different regions [*Liousse et al.*, 1993], which implies that the mass absorption efficiency must be determined experimentally at every site where Aethalometers are used to estimate black carbon concentrations (see 3.3.5.4). Early models of the Aethalometer have a very broad wavelength response, while newer versions offer narrow-band measurements at multiple wavelengths.

Bond et al. [1999] recently characterized the response of another commercial, filter-based instrument for determining τ_{ap} , the Particle/Soot Absorption Photometer (Model PSAP, Radiance Research, Seattle, USA) to laboratory aerosols with different single-scattering albedos, using a calibration standard based on the difference between τ_{ep} , measured with a long-path extinction cell, and τ_{sp} , measured with an integrating nephelometer. They reported systematic errors in the manufacturer's calibration curve for the PSAP, as well as a response from non-absorbing particles. The correction scheme reported by *Bond et al.* [1999] should be applied to all PSAP results from GAW stations. The PSAP operates at a wavelength of 565 nm, but the calibration reported by *Bond et al.* [1999] is for a wavelength of 550 nm.

Yet another filter-based instrument is the Multi-Angle Absorption Photometer (MAAP), produced by Thermo ESM Andersen Instruments (Erlangen, Germany). The MAAP uses a different optical configuration than the Aethalometer and PSAP, with measurements of the filter reflectivity at two different angles in addition to the filter transmission measurement [*Petzold et al.*, 2002]. The two reflectivity measurements allow correction for multiple scattering processes involving the deposited particles and the filter matrix. This approach eliminates the need for a correction scheme based on independent measurements of aerosol light scattering coefficient. The MAAP operates at a wavelength of 670 nm.

Recent improvements in a different approach to determination of aerosol light absorption coefficient, photoacoustic spectroscopy, offer a promising alternative to filter-based methods [Moosmüller *et al.*, 1998; Arnott *et al.*, 2003]. Although not as sensitive, and not yet commercially available, the photoacoustic method allows determination of aerosol light absorption coefficient while the particles are suspended in air, eliminating the artifacts introduced by depositing the particles on a filter. The photoacoustic method can be used in regions where light absorption levels are moderately high, and as a calibration standard for filter-based instruments.

The light absorption measurements should use the same inlet system (humidity- and size-controlled) as the rest of the aerosol sampling system. The filter-based methods yield erratic results when the humidity changes, particularly at high relative humidity [Arnott *et al.*, 2003]. For this reason, a supplemental heater at the inlet of the instrument may be needed to ensure that the sample RH is kept below 50% in air-conditioned laboratories. Routine maintenance needs of the filter-based methods are minimal: (i) change the filter when the amount of transmitted light gets too low (ca. 70% of the initial intensity). The MAAP and some Aethalometer models perform this filter change automatically (ii) check the flowrate and lamp brightness regularly, and (iii) measure the sample area of the filter deposit (considerable unit-to-unit variation has been observed for the PSAP).

4.4 Data Reporting, Sampling Frequency, Data Editing

The time resolution of the records of aerosol optical variables should allow generation of hourly statistics, preferably from integrals taken over 1 to 3 minute periods. These should include arithmetic mean and standard deviation, median, 5%ile, and 95%ile values for each hour. Quality control of data is the responsibility of each observing station, data known to be contaminated or otherwise corrupted should be flagged.

4.5 Quality assurance and quality control considerations (QA/QC)

Suitable aerosol standards do not exist for field audits of the performance of instruments for determining aerosol light scattering and absorption coefficients. Calibration of integrating nephelometers should be checked on a monthly basis by measuring the response of the instrument when filled with a gas whose scattering coefficient is known (carbon dioxide is an appropriate choice). A corresponding method for auditing the calibration of filter-based light absorption instruments does not exist, although highly desirable. Instead, it is recommended that GAW stations operating continuous light absorption photometers operate a travelling laboratory reference instrument calibrated by an appropriate method alongside the first for at least one week, periodically to check for long-term drift in instrument response.

Calibration of internal sensors for measuring flow rate, temperature, pressure, and relative humidity should be performed on an annual basis, and archived

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5. PARTICLE NUMBER CONCENTRATION AND SIZE DISTRIBUTION

5.1 Particle Number Concentration

Particle number or condensation nuclei (CN) concentration represents a single integral measurement of particle number across a wide size range, encompassing several modes in the number size distribution. Such integral particle measurements serve various purposes:

5.1.1 Long-Term Change

Predominantly, CN concentration gives an indication of the instantaneous balance between particle production and removal in the sampled air and hence, CN is responsive to changes in the net result of these processes.

5.1.2 Adjunct to number size distributions

CN concentration is a useful adjunct to the determination of number size distributions, providing a direct measure of the integral over the size range of ambient aerosols. CN is a relatively easily measured variable that can be used to evaluate aerosol dynamics models that predict aerosol particle number size distributions.

5.1.3 Health effects of particles

Numerous epidemiological studies suggest a link between the mass of airborne particles and human health (see for example *Dockery and Pope [1996]*). The number concentration of ultra-fine particles (in this context defined as particles with diameter less than 100 nm) is also considered a possible factor in the adverse impact of airborne particles and human health [*Oberdörster et al., 1995, Seaton et al., 1995*]. In urban and rural air, these ultrafine particles generally comprise the major fraction of the CN number concentration.

5.1.4 Active sampling controller

Because high number concentrations of CN are produced mainly by anthropogenic activities, and in particular combustion processes, CN can be used for active control of other aerosol sampling devices, particularly filter or other time-integrated collectors. In this case, large concentrations of CN, or rapid increases in concentration act as an indicator predominantly for local sources that might otherwise be disproportionately represented in the collected sample. Preferably, the sample time will be one second or less and it may be desirable to operate the controlled collector with an effective delay to enable complete isolation. Various algorithms using CN concentration, and its time derivative, have been developed for sample control; further details can be obtained from the GAW World Calibration Centre for Aerosol Physics WCCAP. However as discussed in 2.4, particle number concentration measurements may not be a reliable control in regions that experience frequent new aerosol particle production events with associated very high particle concentration bursts not associated with local pollution.

5.2 Types of CN measurement and factors to be considered

Condensation nuclei can be detected after the condensation of water, or other condensable vapour (often an alcohol such as butanol) from a supersaturated atmosphere onto the particle. The super saturation in CN counters (CNCs), which are also known as condensation particle counters (CPCs), is typically quite large, around 150%, allowing detection of particles as small as a few nanometers diameter.

Optical methods are usually used to detect the resulting droplets. Early counters relied on manual counting, either in-situ or after photography. The Nolan-Pollak counter [*Metnieks and Pollak, 1959*] and its derivatives (such as the Gardner counter, [*Rich, 1955, Hogan et al., 1975*]) rely

on determination of the optical extinction of the resulting cloud. Photometric observation of light scattered by the droplets is used in some counters. The most satisfactory method is individual counting of particles condensed in a continuous flow, as employed in the family of CNCs that have developed from the design of *Bricard et al.* [1976]. This procedure is employed in most modern commercial CNCs. It has the advantage of giving a “direct” determination of CN concentrations up to about 10^5 cm^{-3} (although this limit is not generally reached by simpler, lower-cost counters).

Long-term stability, accuracy, concentration range, lower size detection threshold and ease of maintenance are major considerations in the selection of a CN counter. Early CN counters were based on batch processing, using expansion to achieve the necessary super saturation (e.g. the Nolan-Pollak counter). These counters, which have a lower size-cut (50% counting efficiency) of around 3 nm diameter, have been used widely in the GAW programme, but are no longer commercially available. Most modern CNCs utilise continuous flow with condensation of an alcohol (typically butan-1-ol) to achieve super saturation and employ single particle counting, although photometric detection is used in some. Flow rates, lower detection diameter and upper concentration ranges, vary between counters; the particular counter used needs to be selected to suit the application.

A continuous CNC with a 10 nm size-cut is recommended as the basic CN instrument for the GAW network (see *Wiedensohler et al.* [1997] for examples of size dependent efficiency of various CNCs or CPCs). Programmes with a wider scientific scope are encouraged to use this basic counter and also include a counter with a lower size-cut of 3 nm (frequently referred to as an ultra-fine counter, thus UCNC or UCPC). The difference of these two measurements is a measure of particle production by nucleation. In locations with large CN concentrations such as urban or polluted areas, the selection of CNCs may need to include a model with upper concentration capacity in excess of 10^5 cm^{-3} (or a dilution system in the sample inlet). However, for GAW global and regional stations such conditions do not normally occur.

5.3 Sampling Inlet and Particle Loss

General inlet design criteria are given elsewhere (Chapter 2). When sampling CN, and particularly ultra-fine CN, it is important to minimise diffusion losses. For CN measurements, any size-selective stages should be by-passed.

5.4 Data Reporting, Sampling Frequency, Data Editing

The time resolution of the CN record should allow generation of hourly statistics, preferably from integrals taken over 1 to 3 minute periods. These should include arithmetic mean and standard deviation, median, 5%ile and 95%ile CN concentration for each hour. Quality control of data is the responsibility of each observing station, data known to be contaminated or otherwise corrupted should be flagged.

5.5 Quality Assurance and Quality Control Plans

To safeguard against unknown malfunction and to ensure maximum coverage, operation of a second CN instrument is recommended preferably with real-time graphic display of the output concentration record. Alternatively, GAW stations operating continuous CN counters should periodically operate a travelling laboratory reference instrument calibrated by an appropriate method alongside the station instrument for at least one week to check for long-term drift in instrument response.

5.6 Particle Number Size Distribution

Measurement of the number size distribution can serve several purposes. At the broadest level, this can be used to infer relative contributions to the aerosol from different sources, such as the presence of strong coarse modes due to mechanical generation processes, or ultrafine modes

due to new particle production from condensation processes. This information is useful in interpretation of the aerosol system in the sampled air mass. For a given location, longer term measurements may be desirable. They can be used to identify aerosol sources especially when combined with aerosol chemistry observations. Size distribution measurements are needed to evaluate regional and global chemical transport and climate models that attempt to include size distributed aerosols as active constituents. Other applications of the number size distribution include: (i) reconciliation of observed cloud condensation nuclei (CCN) through modelling, based on observed particle number and chemical composition size distributions and (ii) explaining observed particle mass in a given size range or observed light-scattering coefficients, all of which are examples of closure studies.

5.7 Instrument Types and Data Reporting

Because of the complexity of the measurement, it is recommended that number size distribution determinations are undertaken only at GAW stations with more highly-developed aerosol programmes. Many commercial instruments are available to do this. They utilise a wide range of physical principles to classify particles according to size. Some of the better known approaches utilise the electrical mobility of particles, aerodynamic size, or optical size determined by light scattering. This latter class includes a number of relatively small, low-cost, instruments utilising laser diodes. Whilst any of these measurement approaches has the potential to add useful data to the overall GAW aerosol measurement programme, it is assumed that stations operating such instrumentation will have a highly developed aerosol programme that includes a documented, calibration and quality control programme.

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6. CLOUD CONDENSATION NUCLEI

6.1 Introduction

Cloud Condensation Nuclei (CCN) measurements are made to determine the concentration and establish climatologies of those particles that have the potential to produce cloud droplets at super saturations typical of natural clouds, that is, less than about 1%. Radiative forcing and precipitation changes through aerosol-cloud interactions represents the largest source of uncertainty in climate prediction [PCC, 2001]. CCN concentration data are important for validation of derived global aerosol climatologies, which form the basis for the derivation of the indirect climate effects of aerosol using global and other climate models.

6.2 Instrument Types

Because of the complexity of the measurement, it is recommended that CCN determinations be undertaken initially only at GAW stations with more highly-developed aerosol programmes. A number of instruments have been developed to measure CCN concentration but at the time of writing there are no known commercial suppliers. This means that use of existing instruments or purpose-built instruments will be necessary. Past CCN measurements in the GAW programme have been made predominantly using static thermal-gradient chambers, which are well-suited to relatively low frequency sampling and low-resolution (differential) CCN spectrum determination. Instruments utilising continuous flow offer another approach, but have yet to be implemented in GAW for more than "process studies". Measurement methods that have available droplet growth times comparable to real clouds are preferable.

6.3 CCN Counter Operation Mode

The recommended standard operation is for continuous measurements at a fixed super saturation of 0.5%. The sampling frequency should be sufficient to allow derivation of hourly statistics (arithmetic mean and standard deviation, median, and 5 and 95%iles). Where feasible, CCN super saturation spectra at super saturations between 0.1 and 1% should be determined. As with the standard mode operation, enough spectra should be produced to allow hourly, or failing this, daily statistics to be calculated and reported.

6.4 Data Reporting, Sampling Frequency, Data Editing

Quality control of data is the responsibility of each observing station, data known to be contaminated or otherwise corrupted should be flagged. Data reporting should include station ID: date, time (UTC), instrument ID and the hourly statistics including error flags. The time resolution of the CCN record should allow generation of hourly statistics. These should include arithmetic mean and standard deviation, median, 5%ile and 95%ile CN concentration for each hour. An operating log should be maintained by the operating agency in which all events related to the CCN counter or inlet system are recorded. A separate log of the calibration history and any servicing of the CCN instrument should be retained by the local organization operating the instrument and copies sent annually to the GAW data centre. Data recording requirements can be obtained from the GAW aerosol data centre or the GAW Aerosol SAG.

6.5 Quality Assurance and Quality Control Plans

A documented calibration and quality control programme is required. Network counters should be regularly calibrated in the field using monodisperse, soluble aerosol of known activity. For CCN active at 0.5% supersaturation for example, this might comprise 150 nm diameter particles of a material such as sodium chloride or ammonium sulphate. Calibration of counting efficiency and measures of supersaturation such as critical diameter should be carried out on a regular, preferably not less than annual, basis. Practices at GAW stations that have experience in

making long-term CCN measurements (e.g. Cape Grim, Australia; Mace Head, Ireland) should be adopted.

6.6 References

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7. AEROSOL OPTICAL DEPTH

7.1 Introduction

Aerosol optical depth (AOD) is a quantitative measure of the extinction of solar radiation by aerosol scattering and absorption between the point of observation and the top of the atmosphere. It is a measure of the integrated columnar aerosol load and the single most important parameter for evaluating direct radiative forcing. AOD can be determined from the ground through measurements of the spectral transmission of solar radiation through the atmosphere using rather simple and relatively inexpensive instruments pointed directly at the sun called sunphotometers or filter radiometers. Routine ground based AOD observations are of utmost importance for the calibration and validation of AOD retrievals from satellites. In addition they are necessary to correct for aerosol effects in the retrieval of other satellite products. The Ångström exponent, which gives an indication of the column integrated aerosol size distribution, can be derived from simultaneous AOD measurements at several wavelengths.

Aerosol optical depth (AOD) is not directly measurable, but rather must be retrieved from observations of atmospheric spectral transmission. The solar irradiance I at a given wavelength can be expressed as $I = I_0 \exp(-md)$ with I_0 the extraterrestrial (top-of-the-atmosphere) irradiance of the sun, m the air mass and d the total optical depth. The air mass equals 1 for a vertical path and is roughly proportional to $1/\cos z$ with z the zenith angle of the sun during the observation. The total optical depth d at a given wavelength is composed of several components such as scattering by gas molecules, d_R (Rayleigh scattering), extinction by aerosol particles, d_A , absorption of trace gases, d_G , like ozone, and possible cloud contamination. Thus, the AOD can be obtained from the total optical depth by subtracting modelled estimates of the other components $d_A = d - d_R - d_G$. Because AOD is essentially a difference between two larger numbers, it is very sensitive to small calibration errors and to a minor degree also to the methods chosen to model the other components. More sophisticated instruments like sky-scanning radiometers can be used to determine other very important optical parameters including single-scattering albedo, phase function or complex index of refraction.

There are many networks measuring AOD on a regional basis as well as two global networks. AERONET [Holben *et al.*, 1998, 2001]) is a major global network with central calibration facilities in the USA and France. It involves a consortium of partners operating up to 100 radiometers on a routine or campaign basis. The Swiss built WMO/GAW precision filter radiometer [Wehrli, 1999; Wehrli, 2000; McArthur *et al.*, 2002] is operating continuously at approximately 12 GAW stations with an instrument expressly designed to make automated long-term trend observations. They will fill gaps in the worldwide network and provide intercomparison information between networks by overlapping at selected sites. It was developed by the World Optical Depth Research Calibration Centre (WORCC) in Davos Switzerland. They are currently overlapping with BSRN [BSRN, 1998], AERONET and other sunphotometers at several sites. There is a need for a common strategy to merge the various network observations into a global data set. It is recommended that GAW work with existing major networks to develop this strategy, implement it and to develop with satellite agencies a system for integrating global AOD observations.

7.2 Method of Measurement and Sampling Frequency

Measurements should be made with sun-pointing direct beam instruments measuring at least at 3 wavelengths from the list of centre wavelengths recommended by WMO [1986]: 368, 412, 500, 675, 778, 862 nm and with a bandwidth of 5 nm. The field-of-view geometry for direct beam radiometers should correspond to the WMO [1996] specifications of a full opening angle of 2.5° and a slope angle of 1° . Measurements should be automated using a sun tracker with a sampling rate of once every minute, as recommended for BSRN [1998] radiation measurements, in order to allow for objective quality control and cloud filtering algorithms. This precludes the use of hand-held sunphotometers.

Few accurate filter radiometer instruments are available commercially. Below, a selection of instruments which have a proven design are given. However, the list is not complete. A sky-scanning radiometer from CIMEL¹ is widely used in the AERONET network. It has 8 channels, to 5 of which are for AOD determination. It comes with a data acquisition and control unit and is mounted on a dedicated sky-scanning robot. A similar instrument with 7 channels is offered by Prede². Both instruments are more sophisticated than traditional sunphotometers in that they also measure sky radiances and are capable of determining the aerosol scattering phase function. Classic filter radiometers are offered by Carter-Scott Design³ or EKO⁴. Another common AOD instrument that is not a direct sunphotometer is the multi-filter rotating shadowband (MFRS) radiometer manufactured by YES⁵ which comes with a data acquisition and control unit and does not need a tracker. All instruments need a PC to read out the data that are stored in the units for several days.

7.3 Calibration

Under conditions of low aerosol loadings, say AOD₅₀₀ of 0.05, a calibration error of 1% can result in an error of 12% for the daily mean AOD and even higher around noontime. WMO has recommended [WMO, 1994] an absolute limit to the estimated uncertainty of 0.02 optical depths for acceptable data and <0.01 as a goal to be achieved in the near future. These specifications require a calibration uncertainty of better than 2% to be maintained for spectral radiometers in daily, operational use. In the past, various attempts to calibrate filter radiometers by spectral irradiance standard lamps in combination with published solar spectra have demonstrated (e.g. [Schmid *et al.*, 1998], that this approach does not meet even the WMO uncertainty limit of 2% with the most severe limitation lying in the discrepancies between different solar spectra. Thus Langley extrapolations, which can achieve a relative uncertainty of 0.5% or better, have remained the current practice for calibration of spectral radiometers used in AOD determination.

Langley extrapolation relies on high temporal and spatial stability of the optical depth during the calibration measurements, conditions that are hardly found at a given observing site, unless at high altitudes, thus inhibiting reliable on-site calibration of individual instruments. Spectral radiometers at GAW stations can be calibrated by comparison to either a travelling standard or to a group of standard radiometers at a regional or world calibration centre. A World Optical Depth Research and Calibration Centre (WORCC) was established in 1996 at the Physikalisch-Meteorologisches Observatorium Davos (PMOD) and is currently setting up a trial AOD network at 12 GAW observatories using newly developed identical precision filter radiometers (PFR) that are traceable to a set of standard instruments maintained at WORCC. Intercomparisons with other, commercially available, instruments have demonstrated (see [McArthur *et al.*, 2003], that the WMO goal of 1994 can indeed be achieved under operational conditions. Intercalibration methods for different instrument types still have to be developed further. Exchange of standardized instruments in a round robin fashion, sometimes used by national or confederated networks like AERONET, would require a common quality assurance strategy.

7.4 Quality Control And Assurance

Quality Control (QC) of a routine AOD observation should include checks of the cleanliness of the optical window, of the accuracy of the solar tracker and, in the case of non-tracking shadowband instruments, checks of the horizontal alignment. All adjustments made or malfunctions detected should be recorded in a logbook and archived together with the raw

¹ CIMEL Electronique, 5 Cité de Phalsbourg, F 75011 Paris, France, <http://www.cimel.fr>

² PREDE Co. , 1117 Kusabana Akiruno-shi, 197-0802 Tokyo, Japan <http://www.prede.com>

³ Carter-Scott Design, 16 Wilson Avenue, Brunswick. Victoria 3056 Australia <http://www.carterscott.com.au>

⁴ EKO Instruments Trading Co, Sasazuka Centre Bldg. 2-1-6, Shibuya-ku, 151-0073 Tokyo, Japan, <http://www.eko.co.jp>

⁵ Yankee Environmental Systems, Inc., 101 Industrial Boulevard, POB 746, Turners Fall, MA 01376, U.S.A., Fax: +1 413 863 0255, <http://www.yesinc.com>

measurements. Further QC involves data screening during the evaluation process, especially flagging measurements for suspected cloud contamination in the line-of-sight. Quality Assurance (QA) for spectral radiometer measurements mainly consists of maintaining proper calibration of the extraterrestrial signals within the required uncertainty of 1-2%. Rotating shadowband radiometers need additional calibration of their directional response function. As filter radiometers tend to show individual ageing effects, it is difficult to recommend a single recalibration interval, which could be twice a year or every two years. Reprocessing of raw data to take instrumental drifts into account is possible to some extent, assuming a linear trend for small changes in calibration.

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8. GAW AEROSOL LIDAR

8.1 Introduction

LIDAR (Light Detection And Ranging) observations of light scattered back by aerosols along a path through the atmosphere traversed by a pulse of laser light are the most promising source of routine information on the spatial distribution of aerosols. Aerosol balloon sondes instruments and aircraft measurements are not yet widely available, less economical and therefore not yet being conducted in many locations. LIDARs operated from ground-based networks are in place now and will soon be in place from satellites. They can complement ground-based in situ or total column aerosol measurements. Ground-based LIDARs fill the ongoing need for insight into the structure of the boundary layer, its height, and its variability with time that is useful in understanding the representativeness of ground-based measurements. Furthermore, information on long-range transport in the free troposphere, cloud observations including cirrus clouds, and knowledge of the vertical distribution of light extinction due to aerosols are essential for understanding the climate role of atmospheric aerosols. For many climate processes (e.g., radiative transfer) altitude-resolved information about aerosols is essential. Satellite observations are only beginning to overcome the deficiency in understanding the distribution of aerosols in the troposphere. Currently satellite observations yield considerable information on AOD over the oceans but less information over land, especially in areas with high surface albedo. There are only a few LIDAR instruments planned for deployment on satellites. In contrast, there are several research LIDAR measurement stations and networks that are well organized with high standards regarding quality control, ongoing development of new controlling measures, and data archival.

In summary, there is a need for systematic measurements of the vertical aerosol distribution and its variations at GAW stations by ground-based LIDAR systems. It is recommended that LIDAR systems should be installed where a comprehensive aerosol programme has been implemented, especially at stations with strong measurement research programmes that support long-term monitoring. The integration of aerosol LIDAR observations with other measurements by radiosonde, ozone sonde, sunphotometer and satellite is most useful allowing for a maximum synergy of information. The informational content of LIDAR observations is greatly enhanced by air parcel trajectory analysis.

8.2 LIDAR Remote Sensing

Remote sensing by LIDAR has received wide application in the space- and time-resolved investigation of atmospheric trace constituents, clouds, wind and temperature since its invention a few decades ago. Today LIDARs are used as ground-based systems, on airborne platforms, and from space (e.g. LITE experiment, [McCormick, 1997]; CALIPSO mission, launch scheduled for 2004, <http://www-calipso.larc.nasa.gov/>). Since the pioneering work by *Fiocco and Grams* [1964] to investigate stratospheric aerosols numerous LIDARs have been built with increasing specialization to meet the growing need in research and environmental control. This relatively young science has now arrived at the point where systems can be designed for certain purposes and built with high reliability and durability. Rapid progress in laser technology, measurement technique, and data acquisition support this development. LIDAR systems for some specific applications are now becoming available commercially.

LIDAR measurements of aerosols may be used in a twofold way when applied at GAW stations: Firstly, they will provide high resolution information on the altitude dependence in the occurrence of tropospheric aerosols, including the retrieval of optical properties such as aerosol backscatter and extinction. Secondly, this information can then be used to derive variations of the atmospheric structure and transport phenomena by interpreting the aerosols as tracers of such variations.

8.3 LIDAR Technique

An aerosol backscatter LIDAR system typically consists of a laser transmitter and an optical receiver in parallel or collinear arrangement. The system transmits intense, short-duration light pulses of linear polarization at a high repetition rate into the atmosphere within the receiver field of view. The intensity of the light elastically backscattered by molecules and particles is measured versus time through the telescope receiver, collimating optics, a narrow bandpass filter for daylight suppression, and an appropriate detector. The signal profile will be stored by a fast analog-to-digital converter or by a photon counting device. Relative intensity data are accumulated separately from all altitude intervals for a selected averaging period, which may include thousands of individual laser shots.

8.3.1 LIDAR Signal Analysis

The single scattering elastic backscatter signal can be expressed by the LIDAR equation

$$S(R) = P C [\beta_M(R) + \beta_P(R)] R^{-2} T^2(R) + B$$

where $S(R)$ is the received signal from a volume at range R , P is the output laser energy, and $\beta_M(R)$ and $\beta_P(R)$ are the molecular and particle (or aerosol) volume backscatter coefficients, respectively. The signal is further a function of range R , and is attenuated by two-way transmission losses T^2 due to light extinction by molecules and particles between transmitter, backscattering volume at range R and the receiver. The constant C includes the pulse repetition rate of the laser, receiver size, and detector sensitivity. B defines background light and instrumental noise.

The signal has to be corrected for detector non-linearity for analog detection systems or pulse pileup for photon-counting systems. In the near-range $S(R)$ is further affected by signal losses due to the incomplete overlap of laser beam and receiver field of view.

Backscatter from atmospheric molecules is defined by the Rayleigh theory. The signal strength of particle backscatter is a function of number density, size distribution, shape and refractive index of the particles, and follows the Mie theory in the case of spherical particles.

8.3.2 Backscatter Retrieval

The LIDAR equation contains the unknowns C , $\beta_P(R)$ and the integral particle extinction in T . Raw data of the backscatter signal will be corrected for background and for range effects, and then adjusted to account for the two-way molecular and aerosol extinction. The particle backscatter signal must be separated from the molecular signal by suitable algorithms. The inversion of the LIDAR equation with respect to particle backscatter $\beta_P(R)$ therefore includes the calculation of the molecular backscatter, the determination of the constant C by normalization of the equation at an altitude with known particle backscatter (or an aerosol-free layer), and the (iterative) determination of the transmission term T . The molecular extinction in T follows the Rayleigh theory, and the aerosol extinction is calculated from the net particle backscatter with assumptions regarding the ratio of aerosol extinction to aerosol backscatter (the LIDAR ratio) (see 8.3.3). Usually altitudes above the investigated aerosol range are sought for normalization, because this far-end calibration leads to a solution more stable than a near-end calibration (e.g. [Klett, 1981; Fernald, 1984; Bissonnette, 1986]).

Molecular backscatter can be calculated from atmospheric pressure and temperature data provided by radiosondes if available. Alternatives are products from a weather forecast model like ECMWF, or surface temperature plus a model atmosphere.

Precision: Uncertainty of aerosol backscatter is lowest in turbid conditions and largest when aerosol scattering is least important.

Accuracy: Molecular profile accuracy and LIDAR ratio accuracy affect the aerosol backscatter profile.

Limitations: Cloudy conditions may lead to receiver overload and severe signal attenuation, and total signal loss is rapidly reached in denser clouds.

8.3.3 Aerosol Extinction

Aerosol extinction retrieval from backscatter data requires height resolved information on the LIDAR ratio or assumptions [Klett, 1985; Carnuth and Reiter, 1986], which in some conditions may be inadequate [Ansmann et al., 1998]. Assumptions of the LIDAR ratio require caution because the ratio may vary from about 20 sr to >120 sr at 532 nm depending on particle composition (refractive index), size distribution, shape, and temperature in case of ice crystals. Importantly, optical depth data from simultaneous sunphotometer measurements can guide the interpretation of LIDAR data.

Aerosol optical depths can also be obtained from multi-elevation-angle measurements with a scanning LIDAR, allowing more accurate determination of extinction profiles. Horizontally inhomogeneous aerosol distributions cause problems, but inconsistent results identify these cases [Gutkowicz-Krusin, 1993; Ansmann et al., 1998].

Very complex LIDAR systems can directly obtain extinction profiles, e.g., the HSRL (High Spectral Resolution LIDAR) technique (e.g., [Piironen and Eloranta, 1994; Hair et al., 1998]) or the nitrogen Raman LIDAR method [Matthias and Bösenberg, 1998], which might be considered in advanced aerosol LIDAR programmes. However, because of the high solar background, the use of inelastic Raman backscatter above 300 nm limits its use mainly to dusk and dawn or night-time measurements [Ansmann et al., 1998].

8.3.4 Depolarization

A GAW aerosol LIDAR system should also include measurements of the polarization properties of atmospheric particles by separating the co-polarized and cross-polarized components of the backscatter return. Spherical particles (e.g. deliquesced hygroscopic salts) do not produce depolarization of the backscattered laser light, whereas crystalline particles (e.g. cirrus ice particles) generate depolarization. The depolarization ratio (ratio of cross-polarized to co-polarized return) provides information on how much the particles deviate from spherical shape. Discrimination between ice and water clouds is the most common application, but depolarization is also used to characterize dust layers and identify other aerosol types like haze or smoke [Sassen, 2000]. LIDAR depolarization can be used to improve aerosol extinction retrieval by helping to identify aerosol types.

8.3.5 Data Products

Raw data products are profiles of total backscatter signals corrected for detector non-linearity, background and range. Primary data products are profiles of the scattering ratio (ratio of calculated molecular backscatter to measured total backscatter), profiles of aerosol backscatter, mixed-layer height, aerosol layers in the free troposphere, cloud base height, depolarization ratio, visible and subvisible cirrus, and detection (night-time) of stratospheric aerosol after major volcanic eruptions. Secondary products are aerosol extinction profiles and optical depth.

8.4 Specifications

All GAW LIDARs should follow the same system philosophy, especially use of the same wavelength(s), eye safe operation, similar sensitivity, similar detection systems, and on-site and remote control. Calibration, data processing, and quality control measures need to be defined and standardized.

Recommended specifications can be summarized as follows: Single, mid-visible wavelength; day and night measurements of backscatter, and depolarization (improved systems); range at least to the tropopause; compact and weather-proof housing; elevation-angle scanning for extinction retrievals and data down to the surface (improved systems).

The sensitivity of the LIDAR should allow the retrieval of tropospheric optical depths in the range 0.02 - 2.0.

Although LIDAR systems meeting all these requirements are not yet commercially produced, the technology is now available. Therefore, specifications are suggested to meet the requirements of the GAW aerosol programme. It is recommended that a GAW LIDAR system should comply with the following specific properties:

PHYSICAL PROPERTIES

- ?? LIDAR: robust, compact, low power consumption, stable optics, easy to adjust, operate, control and maintain.
- ?? Housing: compact with window, window cleaning for unattended operation, weather-proof, humidity and temperature controlled.
- ?? System (at least with some versions) transportable for special studies and intercomparisons.

TRANSMITTER

- ?? Single-wavelength LIDAR.
- ?? Wavelength: in the mid-visible (close to sunphotometer channels).
- ?? Laser: diode pumped Nd:YAG (532 nm) or Nd:YLF (523 nm), high repetition rate and low pulse energy.
- ?? The use of additional wavelengths (e.g., 1064 nm and/or 355 nm) is highly recommended for an advanced aerosol programme together with 2nd generation systems. It has been well established that it is often possible to derive extra information from multi-wavelength backscatter and depolarization data, including particle shape and size.

SAFETY

- ?? Eyesafe emission (from out of the window)

MODE OF OPERATION

- ?? Operation: day and night use, continuous, automated operation.
- ?? Time resolution: averaging period down to minutes.
- ?? Height resolution: 30 m or better.
- ?? Range: from ground to a few kilometres above the tropopause.

SIGNAL

- ?? Backscatter: 1 channel for elastic Rayleigh + Mie backscatter.
- ?? Depolarization (recommended option for improved systems): 2 channels for co-polarized and cross-polarized signal for depolarization measurements.
- ?? Background: accurate measurement of background signal by pre-trigger and/or analysis of data from very far range.
- ?? Continuous LIDAR operation produces large data flows requiring adequate data storage capacities and data reduction.

CLOSE RANGE SIGNAL

- ?? To bring the minimum height for measurements down closer to ground one can add a low-altitude, wide field-of-view channel, or add scanning in elevation angle to near horizontal. Another possibility (though often unstable in practice) is to determine a function to correct for the incomplete overlap of laser beam and telescope field of view in the near-range.

- ?? In case of mountain site stations the LIDAR system should be placed at a lower elevation or nearby valley site for investigations of the entire aerosol column above the station, and for profile interpretations by station data.

COMMUNICATION

- ?? System control: on-site and remote.
?? Data transmission: on-site and remote download (by telephone line or Internet connection).

8.5 Quality Assurance and Quality Control Plans

MEASUREMENT

Blind intercomparison with transportable system.

RETRIEVAL ALGORITHMS

Blind intercomparison of raw data processing using synthetic data.

INTERPRETATION

Intercomparison of secondary products (e.g. extinction profiles, optical depth) with results from integrating systems (e.g. sunphotometers), in situ systems on nearby mountain site or airborne systems (balloon, aircraft) like backscatter sonde, particle counter, etc.

COMPARABLE DATA SETS

In order to produce comparable data sets the application of certified data retrieval algorithms should be strictly requested. The development of such retrieval algorithms within GAW is a prerequisite.

8.6 Eye-Safe LIDAR Systems For Unattended Use

Eye-safe LIDAR systems for unattended use under various environmental conditions have already been developed. Examples are the Depolarization and Backscatter Unattended LIDAR (DABUL) and the Micro Pulse LIDAR (MPL). Both of them experienced extended field use.

The DABUL has been developed at NOAA/ETL [Grund and Sandberg, 1997] for unattended use under arctic and tropical conditions [Intrieri et al., 2001]. This system measures backscatter and depolarization and employs a wide angle mode for near range observations.

The MPL, developed at NASA/GSFC [Lee et al., 1997], is used in a worldwide network. The MPL is a single channel instrument for backscatter measurements, and it is commercially available.

The experience gathered with these and other systems should lead to the development of a GAW LIDAR system at reasonable costs.

8.7 References

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Information can also be found in the following directory and networks:

- ?? International LIDAR Researchers Directory:
<http://www-arb.larc.nasa.gov/lidar/directory.html>
- ?? EARLINET - European Aerosol Research LIDAR Network: <http://lidarb.dkrz.de/>. This LIDAR network will establish an aerosol climatology of the boundary layer, the free troposphere, and the stratosphere at European stations. LIDAR: individually designed advanced LIDAR systems for extinction profile retrievals (Raman, multiple angle, multi wavelength).
- ?? MPL - Network: <http://mplnet.gsfc.nasa.gov/>. Worldwide network of micro-pulse LIDAR (MPL) systems to determine the vertical structure of clouds and aerosols. All MPL-Net sites are collocated with sunphotometers, which are used to calibrate LIDAR measurements. LIDAR: single channel system, autonomous, eye-safe and commercially available.
- ?? AD - Net: <http://info.nies.go.jp:8094/kosapub/>. East Asian LIDAR network to investigate the springtime transport of Asian dust. LIDAR: depolarization and high-spectral-resolution LIDARs.

9. ARCHIVING PROCEDURES

9.1 Introduction

The procedures, and data archiving requirements described below have been adopted by the World Data Centre for Aerosols (WDCA) to address the following features and requirements of the GAW aerosol measurement programme described in chapter 1.

1. ***“The objective of the GAW aerosol component is to determine the spatio-temporal distribution of aerosol properties related to climate forcing and air quality at up to multi-decadal time scales”.***

The long-term nature of the GAW measurement programme makes it imperative that adequate meta-data are maintained together with the observational data, as several decades after a measurement has been made it will not always be possible to contact the original investigator in person. The data submission requirements of the WDCA thus place a strong emphasis on meta-data to provide a complete description of the dataset including its quality. The philosophy of the WDCA is to always encourage data users to contact the original investigator to discuss with them the sensible use of their data, while also collecting sufficient meta-data to enable continued use of the data, when this is no longer possible.

2. ***“Since the residence time of aerosol particles is relatively short a large number of measuring stations is needed globally”.***

A global synthesis of aerosol data from GAW and contributing partner networks requires efficient data exchange. WDCA has therefore adopted a flexible data exchange standard and is working with partners to support easy use and exchange of aerosol data from other networks together with those from GAW.

3. ***“The data available from WDCA should be of a known quality and include all information required by a user to permit sensible use of the data”.***

The WDCA requires processed data submitted to it to be of a known and demonstrable quality. Every data record therefore carries one of a standard set of data quality flags. The data file and the data tables within the file contain sufficient meta-data, including contact details for the data originator and acknowledgement instructions for data users, to encourage sensible use of the data.

9.2 The NARSTO data exchange standard

WDCA has adopted the NARSTO Data Exchange Standard (DES) for both submission of data to the data centre and provision of data to the public. NARSTO, (originally "North American Research Strategy for Tropospheric Ozone,") is a tri-national (Canada, Mexico and the USA), public-private partnership for researching multiple features of tropospheric pollution, including ozone and suspended particulate matter.

The Data Exchange Standard (DES) developed by NARSTO uses ASCII standard characters and comma separated values within each data record. Files meeting the DES can thus be read and written by proprietary spreadsheet and database applications. A file that conforms to the DES contains:

- ?? A file header containing the metadata relevant to the entire data file
- ?? A data table containing the NARSTO standard flags used to flag individual observed variables in the records in the main data table (mandatory)
- ?? A data table containing the site details for all sites containing (mandatory)
- ?? Optional data tables describing for example data flags used by the organization and their NARSTO standard equivalents,
- ?? A main data table containing the time series of observational data for a particular parameter and time interval.

A data table is comprised of a number of columns of data each of which are identified by a number of rows of column headers which are phrases (name, format type, format, missing code, etc.) which describe the data in that column, followed by the rows of data themselves. For most of these meta-data key phrases look-up tables of allowable names are available to aid the user. A benefit of defining the valid options for the key phrases that describe the data is that files can be analysed automatically to check that they conform to the DES.

Documentation on the most recent version of the DES is available from the NARSTO Quality Systems Science Centre (QSSC) at Oak Ridge National Laboratory (<http://cdiac.esd.ornl.gov/programs/NARSTO/narsto.html>).

The first time user of the DES should download and use the [data exchange template](#) from the NARSTO QSSC above. This is an Excel application that contains detailed instructions on how to complete the template, together with the template itself, which is extensively annotated and contains drop-down lists of options for many of the key phrases, example DES files for Aerosol Chemistry and Light Scattering measurements and a sheet of Frequently Asked Questions.

9.3 Data flow from the data provider to the data user

Here an overview of the typical data flows from GAW stations to the WDCA and onwards from WDCA to data users are described, depending upon whether or not the individual station is submitting data directly to WDCA or is doing so indirectly via a secondary data submission from the data centre of a contributing partner network. The latter is the case for data submission from sites in Europe, where the Chemical Co-ordinating Centre (CCC) of the European Monitoring and Evaluation Programme (EMEP) will co-ordinate primary data submission from both GAW and EMEP sites. A schematic representation of the alternative data flows is shown in Figure 9.1.

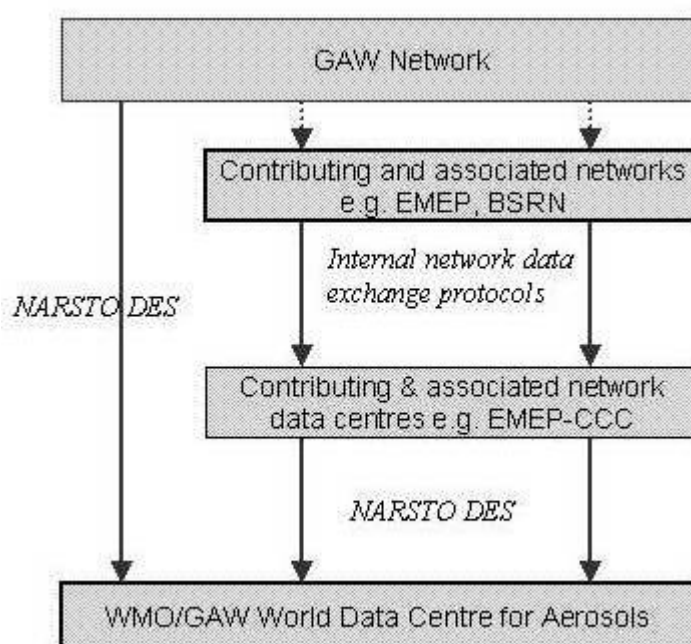


Figure 9.1: Schematic representation of direct and secondary data flow from GAW sites and contributing networks to data centres and the WDCA.

9.3.1 Direct data submission

For direct data submission to WDCA the following steps should be taken:

1. The first time data supplier should contact WDCA about the data that they wish to submit and obtain a copy of the DES template.
2. A specimen of the template, with a small amount of data should then be filled in, with the assistance of WDCA.
3. This file is then run through the WDCA 'read and verify' programme, which makes a large number of internal consistency checks (e.g. all key phrases are 'correct, no required information is missing, data formats are correctly described, the local to UTC time conversions are correct, the data series is sequential, missing values are correctly identified etc.).
4. Once all errors identified by the read and verify programme have been removed, the data supplier, may either use the resulting DES compliant template to generate longer time series of data for submission or use other software to reproduce the DES compliant file. These files should be stored in CSV format and submitted to WDCA.
5. The submitted files are run through the read and verify software. If they are passed, then a quality assured version of the file including an extra table of summary statistics is generated and this is the copy of the data that is made available to the public.
6. Higher level processing of the data to produce, for example time series plots and synthesis products from several sites, such as maps follows on from the successful completion of stage 5.

The data flow for direct data submission is illustrated in Figure 9.2.

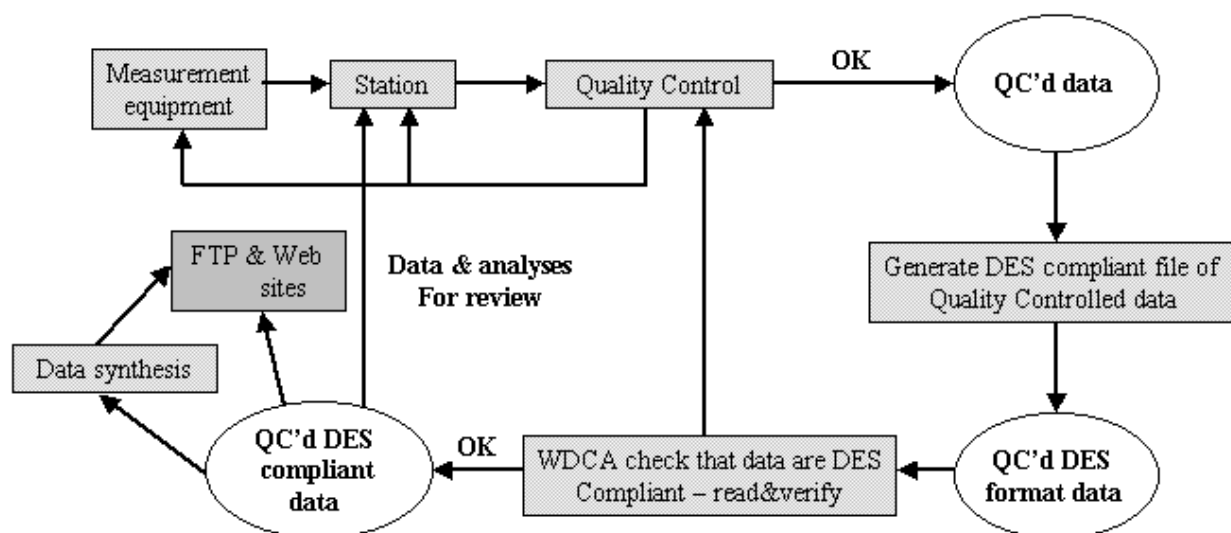


Figure 9.2: Typical data flow from sites to WDCA to data users in the case of direct data submission to WDCA.

9.3.2 Secondary data submission

The data flow for secondary data submission for data originating from a contributing network such as EMEP or BSRN, is illustrated in Figure 9.3. The difference between direct and secondary data submission is that in the case of direct data submission the GAW site is responsible for preparation of the data in the NARSTO data exchange standard, and WDCA liaises with the site to resolve any data quality issues, whereas for secondary data submission, the normal data submission protocols for the network are used for data submission from the site to the network data centre, and the network data centre is responsible for submitting data from the entire

network to WDCA in the NARSTO data exchange standard. WDCA then liaises with the network data centre to resolve any data quality issues.

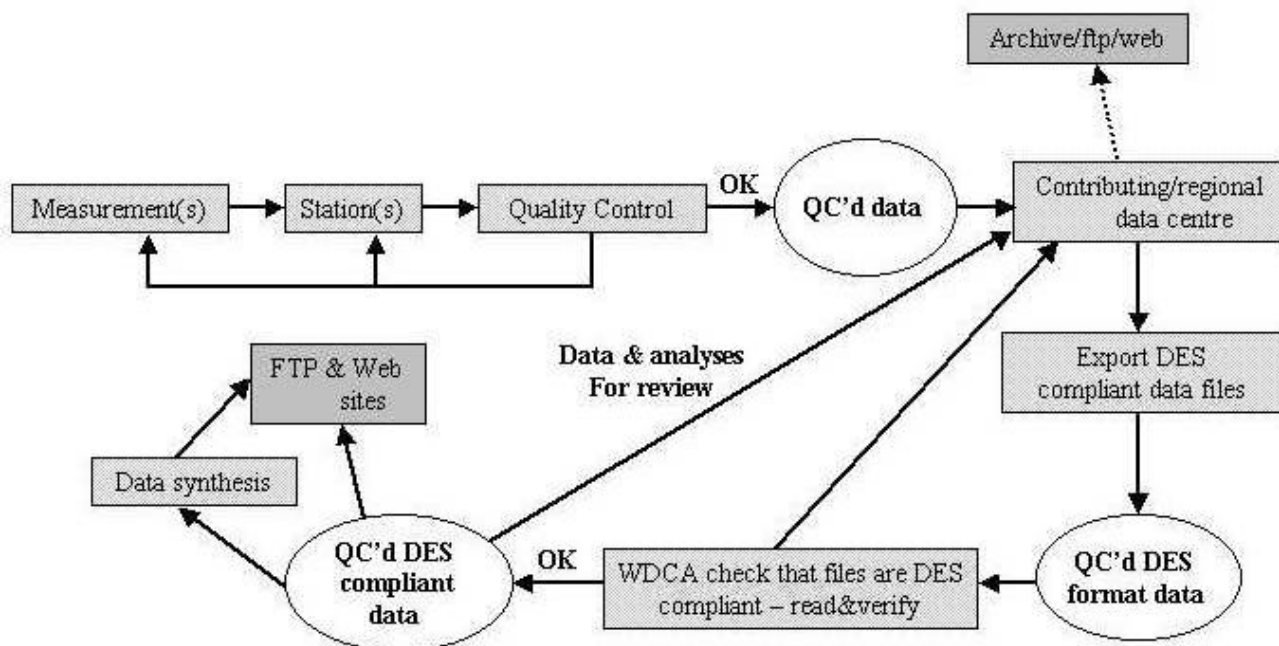


Figure 9.3. Typical data flow from sites to WDCA to data users in the case of secondary data submission to WDCA via a contributing network

Data descriptions and Meta-data

As the data exchange template and associated documentation available from the NARSTO QSSC provide all the information necessary for someone to compile a DES file, the following sections contain lists of the meta-data that needs to be provided with each file and table within the file, and are to be consulted in conjunction with a copy of the data exchange template.

A DES file contains two types of meta-data: a header of file specific meta-data and table specific meta-data, which describe the content of individual tables.

A1.1 File Header meta-data

The following key fields of meta-data form the header of a standard NARSTO DES file. In a completed file the key phrases below are found in the first column, with the actual meta-data in the following column or columns. Detailed instructions on how to fill in the key fields are found in the data exchange template:

*DATA EXCHANGE STANDARD VERSION	<i>mandatory</i>
*COMMENT	<i>optional</i>
*QUALITY CONTROL LEVEL	<i>mandatory</i>
*DATE THIS FILE GENERATED/ARCHIVE VERSION NUMBER	<i>mandatory</i>
*ORGANIZATION ACRONYM	<i>mandatory</i>
*ORGANIZATION NAME	<i>mandatory</i>
*STUDY OR NETWORK ACRONYM	<i>mandatory</i>
*STUDY OR NETWORK NAME	<i>mandatory</i>
*FILE CONTENTS DESCRIPTION--SHORT/LONG	<i>mandatory</i>
*PRINCIPAL INVESTIGATOR NAME--LAST/FIRST	<i>mandatory</i>
*PRINCIPAL INVESTIGATOR AFFILIATION	<i>mandatory</i>
*CO-INVESTIGATOR NAME--LAST/FIRST	<i>optional</i>
*CO-INVESTIGATOR AFFILIATION	<i>optional</i>
*COUNTRY CODE	<i>mandatory</i>
*STATE OR PROVINCE CODE	<i>mandatory</i>
*SAMPLING INTERVAL AS REPORTED IN MAIN TABLE	<i>mandatory</i>
*SAMPLING FREQUENCY OF DATA IN MAIN TABLE	<i>mandatory</i>
*PRINCIPAL INVESTIGATOR CONTACT INFORMATION	<i>mandatory</i>
*DATA USAGE ACKNOWLEDGEMENT	<i>mandatory</i>
*NAME AND AFFILIATION OF PERSON WHO GENERATED THIS FILE	<i>mandatory</i>
*DATE OF LAST MODIFICATION TO DATA IN MAIN TABLE	<i>mandatory</i>
*FILE CHANGE HISTORY--VERSION NUMBER/DESCRIPTION	<i>mandatory</i>
*NAME AND VERSION OF SOFTWARE USED TO CREATE THIS FILE	<i>mandatory</i>
*STANDARD CHARACTERS	<i>mandatory</i>
*COMPANION FILE NAME/FORMAT AND VERSION	<i>optional</i>

A1.2 Table meta-data

The following table column key fields are the full range of possible column meta-data key phrases that can be used for a data table. Seven of them are mandatory for all tables types (flags, station information and data), while the remaining key phrases are either mandatory for the data table, or optional. The latter should be used where they are applicable to some or all of the columns and left out when they are not applicable to any column. Again full instructions on which phrases to include and which to leave out are included in the DES template file.

*TABLE NAME	<i>mandatory for all tables</i>
*TABLE FOCUS	<i>mandatory for all tables</i>
*TABLE EXPLANATION OF ZERO OR NEGATIVE VALUES	<i>mandatory for data table</i>
*TABLE EXPLANATION OF REPORTED DETECTION LIMIT VALUES	<i>mandatory for data table</i>
*TABLE EXPLANATION OF REPORTED UNCERTAINTY	<i>mandatory for data table</i>
*TABLE USER NOTE	<i>optional for all tables</i>
*TABLE KEY FIELD NAMES	<i>mandatory for data table</i>
*TABLE COLUMN NAME	<i>mandatory for all tables</i>
*TABLE COLUMN NAME TYPE	<i>mandatory for data tables</i>
*TABLE COLUMN CAS IDENTIFIER	<i>mandatory for data tables</i>
*TABLE COLUMN EXPLANATION OF DERIVED VARIABLE	<i>optional for all tables</i>
*TABLE COLUMN USER NOTE	<i>optional for all tables</i>
*TABLE COLUMN UNITS	<i>mandatory for all tables</i>
*TABLE COLUMN FORMAT TYPE	<i>mandatory for all tables</i>
*TABLE COLUMN FORMAT FOR DISPLAY	<i>mandatory for all tables</i>
*TABLE COLUMN MISSING CODE	<i>mandatory for all tables</i>
*TABLE COLUMN LOOKUP TABLE NAME	<i>mandatory for data tables</i>
*TABLE COLUMN OBSERVATION TYPE	<i>mandatory for data tables</i>
*TABLE COLUMN FIELD SAMPLING OR MEASUREMENT PRINCIPLE	<i>mandatory for data tables</i>
*TABLE COLUMN PARTICLE DIAMETER--LOWER BOUND (UM)	<i>optional for data tables</i>
*TABLE COLUMN PARTICLE DIAMETER--UPPER BOUND (UM)	<i>optional for data tables</i>
*TABLE COLUMN PARTICLE DIAMETER--MEDIAN (UM)	<i>optional for data tables</i>
*TABLE COLUMN MEDIUM	<i>optional for data tables</i>
*TABLE COLUMN COATING OR ABSORBING SOLUTION/MEDIA	<i>optional for data tables</i>
*TABLE COLUMN WAVELENGTH (NM)	<i>optional for data tables</i>
*TABLE COLUMN WAVELENGTH--LOWER BOUND (NM)	<i>optional for data tables</i>
*TABLE COLUMN WAVELENGTH--UPPER BOUND (NM)	<i>optional for data tables</i>
*TABLE COLUMN SAMPLING HEIGHT ABOVE GROUND (M)	<i>mandatory for data tables</i>
*TABLE COLUMN INLET TYPE	<i>optional for data tables</i>
*TABLE COLUMN SAMPLING HUMIDITY OR TEMPERATURE CONTROL	<i>optional for data tables</i>
*TABLE COLUMN LABORATORY ANALYTICAL METHOD	<i>optional for data tables</i>
*TABLE COLUMN SAMPLE PREPARATION	<i>optional for data tables</i>
*TABLE COLUMN BLANK CORRECTION	<i>optional for data tables</i>
*TABLE COLUMN VOLUME STANDARDIZATION	<i>optional for data tables</i>
*TABLE COLUMN INSTRUMENT NAME AND MODEL NUMBER	<i>optional for data tables</i>
*TABLE COLUMN MEASUREMENT PRINCIPAL INVESTIGATOR	<i>optional for data tables</i>
*TABLE COLUMN DETECTION LIMIT	<i>optional for data tables</i>

A1.3 Data flags

The data table describing the NARSTO standard flags follows the header meta-data records. The standard flags and their definitions are given below. Each observed variable in a data record is required to have a data flag.

*TABLE NAME	NARSTO standard flags	
*TABLE FOCUS	Metadata	
*TABLE COLUMN NAME	Flag: NARSTO	Description
*TABLE COLUMN UNITS	None	None
*TABLE COLUMN FORMAT TYPE	Char	Char
*TABLE COLUMN FORMAT FOR DISPLAY	2	120
*TABLE BEGINS		
	V0	Valid value
	V1	Valid value but comprised wholly or partially of below detection limit data
	V2	Valid estimated value
	V3	Valid interpolated value
	V4	Valid value despite failing to meet some QC or statistical criteria
	V5	Valid value but qualified because of possible contamination (e.g., pollution source, laboratory contamination source)
	V6	Valid value but qualified due to non-standard sampling conditions (e.g., instrument malfunction, sample handling)
	V7	Valid value but set equal to the detection limit (DL) because the measured value was below the DL
	M1	Missing value because no value is available
	M2	Missing value because invalidated by data originator
	H1	Historical data that have not been assessed or validated
*TABLE ENDS		

A1.4 Site Information Table

The site information table has a very similar structure to the NARSTO standard flags table. Whereas the flags table contains two columns (Flag: NARSTO and Description), it contains the following columns for each site where data is provided in the main data table. The site information table is normally found after the NARSTO standard flags table within a file.

Site ID: standard	<i>mandatory</i>
Site abbreviation: standard	<i>mandatory</i>
Description	<i>optional</i>
Country code	<i>mandatory</i>
State or province code	<i>mandatory</i>
Latitude: decimal degrees	<i>mandatory</i>
Longitude: decimal degrees	<i>mandatory</i>
Lat/lon reference datum	<i>mandatory</i>
Sampling height above ground	<i>optional</i>
Ground elevation: above mean sea level	<i>mandatory</i>
Pressure: site ground level	<i>optional</i>
Site land use	<i>mandatory</i>
Site location setting	<i>mandatory</i>
Measurement start date at site	<i>mandatory</i>
Measurement end date at site	<i>mandatory</i>
Co-incident measurements at site	<i>optional</i>
Site ID: study	<i>optional</i>
Lat/lon accuracy	<i>optional</i>

Lat/lon method	<i>optional</i>
AIRS ID	<i>optional</i>
City/town	<i>optional</i>
County/WMO region	<i>mandatory</i>
WDCA/GAW station type	<i>mandatory</i>
GAWID	<i>mandatory</i>
Comment	<i>optional</i>

A1.5 Main data table

The main data tables for each of the aerosol parameters share a number of common features. The first 11 columns of the data record are

- ?? Site ID: standard
- ?? Instrument co-location ID
- ?? Date start: local time
- ?? Time start: local time
- ?? Date end: local time
- ?? Time end: local time
- ?? Time zone: local
- ?? Date start: UTC
- ?? Time start: UTC
- ?? Date end: UTC
- ?? Time end: UTC

These are then followed by the parameter specific measured variables with their associated flags, additional derived variables and or statistics, for which flags are not necessary.

In the following sections details of the variables, derived parameters and statistics that may be reported together with the usual table column key phrases used in the main data table to report each measurement are given.

A1.5.1 Aerosol Chemistry

For Aerosol Chemistry each component analysed (e.g. sulphate, nitrate, chloride, sodium, ammonium ion etc.) together with its associated flag should be reported together with the volume of air sampled, again with a flag, where recorded.

The following column key phrases will normally to be used in the main data table:

- *TABLE NAME
- *TABLE FOCUS
- *TABLE EXPLANATION OF ZERO OR NEGATIVE VALUES
- *TABLE EXPLANATION OF REPORTED DETECTION LIMIT VALUES
- *TABLE EXPLANATION OF REPORTED UNCERTAINTY
- *TABLE USER NOTE
- *TABLE KEY FIELD NAMES
- *TABLE COLUMN NAME
- *TABLE COLUMN NAME TYPE
- *TABLE COLUMN CAS IDENTIFIER
- *TABLE COLUMN UNITS
- *TABLE COLUMN FORMAT TYPE
- *TABLE COLUMN FORMAT FOR DISPLAY
- *TABLE COLUMN MISSING CODE
- *TABLE COLUMN LOOKUP TABLE NAME
- *TABLE COLUMN OBSERVATION TYPE
- *TABLE COLUMN FIELD SAMPLING OR MEASUREMENT PRINCIPLE

- *TABLE COLUMN PARTICLE DIAMETER--LOWER BOUND (UM)
- *TABLE COLUMN PARTICLE DIAMETER--UPPER BOUND (UM)
- *TABLE COLUMN MEDIUM
- *TABLE COLUMN COATING OR ABSORBING SOLUTION/MEDIA
- *TABLE COLUMN SAMPLING HEIGHT ABOVE GROUND (M)
- *TABLE COLUMN INLET TYPE
- *TABLE COLUMN SAMPLING HUMIDITY OR TEMPERATURE CONTROL
- *TABLE COLUMN LABORATORY ANALYTICAL METHOD
- *TABLE COLUMN SAMPLE PREPARATION
- *TABLE COLUMN BLANK CORRECTION
- *TABLE COLUMN VOLUME STANDARDIZATION
- *TABLE COLUMN INSTRUMENT NAME AND MODEL NUMBER

A1.5.2 In-situ Measurements of Aerosol Radiative Properties

For light scattering observations, hourly mean data are normally to be reported. The mean light scattering coefficient at each wavelength observed, together with it's associated flag should be reported, at each wavelength that the instrument operates. For instruments additionally measuring the backscatter coefficient, this should also be reported, with flag, at each wavelength. Additionally the mean internal temperature, pressure and relative humidity of the instrument during the hour, may be reported as supplementary data. These do not require flags.

The following column key phrases will normally to be used in the main data table:

- *TABLE NAME
- *TABLE FOCUS
- *TABLE EXPLANATION OF ZERO OR NEGATIVE VALUES
- *TABLE EXPLANATION OF REPORTED DETECTION LIMIT VALUES
- *TABLE EXPLANATION OF REPORTED UNCERTAINTY
- *TABLE KEY FIELD NAMES
- *TABLE COLUMN NAME
- *TABLE COLUMN NAME TYPE
- *TABLE COLUMN UNITS
- *TABLE COLUMN FORMAT TYPE
- *TABLE COLUMN FORMAT FOR DISPLAY
- *TABLE COLUMN MISSING CODE
- *TABLE COLUMN LOOKUP TABLE NAME
- *TABLE COLUMN OBSERVATION TYPE
- *TABLE COLUMN FIELD SAMPLING OR MEASUREMENT PRINCIPLE
- *TABLE COLUMN PARTICLE DIAMETER--LOWER BOUND (UM)
- *TABLE COLUMN PARTICLE DIAMETER--UPPER BOUND (UM)
- *TABLE COLUMN WAVELENGTH (NM)
- *TABLE COLUMN SAMPLING HEIGHT (M AGL)
- *TABLE COLUMN INLET TYPE
- *TABLE COLUMN SAMPLING HUMIDITY OR TEMPERATURE CONTROL
- *TABLE COLUMN BLANK CORRECTION
- *TABLE COLUMN VOLUME STANDARDIZATION
- *TABLE COLUMN INSTRUMENT NAME AND MODEL NUMBER

For light absorption and equivalent black carbon concentrations, hourly mean data are normally to be reported. The light absorption coefficient and flag should be reported. Additionally, the equivalent black carbon concentration and flag may be reported. In this case, the filter cross section area, dilution factor, light absorption correction factor, and specific absorption coefficient used to derive the black carbon concentration from the light absorption measurement should be reported, either in each record, or as a TABLE USER COMMENT field for the equivalent black carbon concentration column.

The following column key phrases will normally to be used in the main data table:

- *TABLE NAME
- *TABLE FOCUS
- *TABLE EXPLANATION OF ZERO OR NEGATIVE VALUES
- *TABLE EXPLANATION OF REPORTED DETECTION LIMIT VALUES
- *TABLE EXPLANATION OF REPORTED UNCERTAINTY
- *TABLE KEY FIELD NAMES
- *TABLE COLUMN NAME
- *TABLE COLUMN NAME TYPE
- *TABLE COLUMN EXPLANATION OF DERIVED VARIABLE
- *TABLE COLUMN USER NOTE
- *TABLE COLUMN UNITS
- *TABLE COLUMN FORMAT TYPE
- *TABLE COLUMN FORMAT FOR DISPLAY
- *TABLE COLUMN MISSING CODE
- *TABLE COLUMN LOOKUP TABLE NAME
- *TABLE COLUMN OBSERVATION TYPE
- *TABLE COLUMN FIELD SAMPLING OR MEASUREMENT PRINCIPLE
- *TABLE COLUMN PARTICLE DIAMETER--LOWER BOUND (UM)
- *TABLE COLUMN PARTICLE DIAMETER--UPPER BOUND (UM)
- *TABLE COLUMN MEDIUM
- *TABLE COLUMN WAVELENGTH (NM)
- *TABLE COLUMN SAMPLING HEIGHT ABOVE GROUND (M)
- *TABLE COLUMN INLET TYPE
- *TABLE COLUMN SAMPLING HUMIDITY OR TEMPERATURE CONTROL
- *TABLE COLUMN BLANK CORRECTION
- *TABLE COLUMN VOLUME STANDARDIZATION
- *TABLE COLUMN INSTRUMENT NAME AND MODEL NUMBER

A1.5.3 Condensation Nuclei

The hourly mean condensation nuclei concentration and flag should normally be reported, additionally the following statistics: standard deviation, median, minimum, maximum, and number of measurements in the hour long sample may be reported.

The following column key phrases will normally to be used in the main data table:

- *TABLE NAME
- *TABLE FOCUS
- *TABLE EXPLANATION OF ZERO OR NEGATIVE VALUES
- *TABLE EXPLANATION OF REPORTED DETECTION LIMIT VALUES
- *TABLE EXPLANATION OF REPORTED UNCERTAINTY VALUES
- *TABLE KEY FIELD NAMES
- *TABLE COLUMN NAME
- *TABLE COLUMN NAME TYPE
- *TABLE COLUMN CAS IDENTIFIER
- *TABLE COLUMN EXPLANATION OF DERIVED VARIABLE
- *TABLE COLUMN UNITS
- *TABLE COLUMN FORMAT TYPE
- *TABLE COLUMN FORMAT FOR DISPLAY
- *TABLE COLUMN MISSING CODE
- *TABLE COLUMN LOOKUP TABLE NAME
- *TABLE COLUMN OBSERVATION TYPE
- *TABLE COLUMN FIELD SAMPLING OR MEASUREMENT PRINCIPLE
- *TABLE COLUMN PARTICLE DIAMETER--LOWER BOUND (UM)
- *TABLE COLUMN PARTICLE DIAMETER--UPPER BOUND (UM)

- *TABLE COLUMN SAMPLING HEIGHT (M AGL)
- *TABLE COLUMN INLET TYPE
- *TABLE COLUMN SAMPLING HUMIDITY OR TEMPERATURE CONTROL
- *TABLE COLUMN BLANK CORRECTION
- *TABLE COLUMN VOLUME STANDARDIZATION
- *TABLE COLUMN INSTRUMENT NAME AND MODEL NUMBER

A1.5.4 Cloud Condensation Nuclei

The same reporting requirements as for condensation nuclei are to be used for cloud condensation nuclei concentrations i.e. hourly means with flag, plus optional statistics. The column key phrases to be used are also the same as for condensation nuclei concentrations.

A1.5.5 Aerosol Optical Depth

The hourly mean aerosol optical depth and flag together with the median, standard deviation and number of observations for the hour, at each wavelength measured by the instrument, should normally be reported for all hours with a meaningful sample of observations.

The following column key phrases will normally to be used in the main data table:

- *TABLE NAME
- *TABLE FOCUS
- *TABLE EXPLANATION OF ZERO OR NEGATIVE VALUES
- *TABLE EXPLANATION OF REPORTED DETECTION LIMIT VALUES
- *TABLE EXPLANATION OF REPORTED UNCERTAINTY
- *TABLE KEY FIELD NAMES
- *TABLE COLUMN NAME
- *TABLE COLUMN NAME TYPE
- *TABLE COLUMN EXPLANATION OF DERIVED VARIABLE
- *TABLE COLUMN USER NOTE
- *TABLE COLUMN UNITS
- *TABLE COLUMN FORMAT TYPE
- *TABLE COLUMN FORMAT FOR DISPLAY
- *TABLE COLUMN MISSING CODE
- *TABLE COLUMN LOOKUP TABLE NAME
- *TABLE COLUMN OBSERVATION TYPE
- *TABLE COLUMN FIELD SAMPLING OR MEASUREMENT PRINCIPLE
- *TABLE COLUMN WAVELENGTH (NM)
- *TABLE COLUMN SAMPLING HEIGHT ABOVE GROUND (M)
- *TABLE COLUMN INSTRUMENT NAME AND MODEL NUMBER

A1.5.5 GAW Aerosol Lidar

No recommendations exist for the submission of GAW aerosol LIDAR to date. The NARSTO DES in it's current form may not be appropriate as some spreadsheets are restricted to a maximum of 256 columns, which may not be sufficient for a single LIDAR record. Potential data providers are therefore urged to work together with the Aerosol SAG; WDCA to develop an appropriate data exchange standard for this parameter.

Acronyms

AAS	Atomic Absorption Spectroscopy
AERONET	AErosol RObotic NETwork
AOD	Aerosol Optical Depth
ASCII	American Standard Code for Information Interchange
DABUL	Depolarization And Backscatter Unattended LIDAR
BAPMoN	Background Air Pollution Monitoring Network
BSRN	Baseline Surface Radiation Network
CALIPSO	Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observations
CCN	Cloud Condensation Nuclei
CN	Condensation Nuclei also known as Condensation Particles (CP)
CNC	Condensation Nucleus Counter
CMDL	Climate Monitoring and Diagnostics Laboratory (U.S.A.)
CP	Condensation Particles, see CN
CPC	Condensation Particle Counter
CPI	Carbon Preference Index
DES	Data Exchange Standard
DMS	Dimethylsulphide
EARLINET	European Aerosol Research Lidar Network
ETL	Environmental Technology Laboratory (U.S.A.)
EU	European Union
FID	Flame Ionization Detector
FR	Filter Radiometer
FWHM	Full Width at Half Maximum
GAW	Global Atmospheric Watch
GSFC	Goddard Space Flight Centre (U.S.A.)
IC	Ion Chromatography
ICPMS	Inductively-Coupled Plasma Mass Spectrometry
INAA	Instrumental Neutron Activation Analysis
JRC	Joint Research Centre (EU – Italy)
LIDAR	Light Detection and Ranging
LITE	Lidar In-space Technology Experiment
MAAP	Multi-Angle Absorption Photometer
MSA	Methane Sulphonic Acid
MPL	Micro Pulse LIDAR
MFRSR	Multi-Filter Rotating Shadowband Radiometer
NARSTO	North American Research Strategy for Tropospheric Ozone
NDIR	Non-Dispersive Infrared
NIOSH	National Institute of Occupational Safety and Health (U.S.A.)
NIST	National Institute of Standards and Technology (U.S.A.)
NOAA	National Oceanic and Atmospheric Administration (U.S.A.)
NSS	Non-Sea Salt
PESA	Proton Elastic Scattering Analysis
PFR	Precision Filter Radiometer
PIXE	Proton Induced X-ray Emission
PMOD	Physical and Meteorological Observatory Davos (Switzerland)
PM	Particulate Matter
PM 2.5	Particulate Matter larger than 2.5 µm aerodynamic diameter
PM 10	Particulate Matter larger than 10 µm aerodynamic diameter
PSAP	Particle/Soot Absorption Photometer
QA	Quality Assurance
QC	Quality Control

QSSC	Quality System Science Centre (U.S.A.)
RH	Relative Humidity
SAG	Science Advisory Group
SOP	Standard Operating Procedure
TEOM	Tapered Element Oscillating Microbalance
TC	Total Carbon Mass
OC	Organic Carbon Mass
BC	Black Carbon Mass (optical analysis)
EC	Elemental Carbon Mass (thermal analysis)
TOT	Thermal Optical Transmission
UCPC	Ultrafine Condensation Particle Counter
UTC	Universal Time Coordinated
WCC	World Calibration Centre
WCCAC	World Calibration Centre for Aerosol Chemistry
WCCAP	World Calibration Centre for Aerosol Physics
WDCA	World Data Centre for Aerosols
WMO	World Meteorological Organization
WORCC	World Optical Depth Research Calibration Centre
XAD	eXperimental ADsorbent (a styrene divinylbenzene polymer)
XRF	X-Ray Fluorescence

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42. Scripps reference gas calibration system for carbon dioxide-in-air standards: revision of 1985 by C.D. Keeling, P.R. Guenther and D.J. Moss. September 1986 (TD No. 125)
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44. Report of the Sixth Session of the WMO Executive Council Panel of Experts on Environmental Pollution, Geneva, 5-9 May 1986. March 1987
45. Proceedings of the International Symposium on Integrated Global Monitoring of the State of the Biosphere (Volumes I-IV), Tashkent, USSR, 14-19 October 1985. December 1986 (TD No. 151)
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47. Procedures and Methods for Integrated Global Background Monitoring of Environmental Pollution by F.Ya. Rovinsky, USSR and G.B. Wiersma, USA. August 1987 (TD No. 178)
48. Meeting on the Assessment of the Meteorological Aspects of the Third Phase of EMEP IIASA, Laxenburg, Austria, 30 March - 2 April 1987. February 1988
49. Proceedings of the WMO Conference on Air Pollution Modelling and its Application (Volumes I-III), Leningrad, USSR, 19-24 May 1986. November 1987 (TD No. 187)
50. Provisional Daily Atmospheric Carbon Dioxide Concentrations as Measured at BAPMoN Sites for the Year 1985. December 1987 (TD No. 198)
51. Report of the NBS/WMO Expert Meeting on Atmospheric CO₂ Measurement Techniques, Gaithersburg, USA, 15-17 June 1987. December 1987
52. Global Atmospheric Background Monitoring for Selected Environmental Parameters. BAPMoN Data for 1985. Volume I: Atmospheric Aerosol Optical Depth. September 1987
53. WMO Meeting of Experts on Strategy for the Monitoring of Suspended Particulate Matter in BAPMoN - Reports and papers presented at the meeting, Xiamen, China, 13-17 October 1986. October 1988

54. Global Atmospheric Background Monitoring for Selected Environmental Parameters. BAPMoN Data for 1983, Volume II: Precipitation chemistry, continuous atmospheric carbon dioxide and suspended particulate matter (TD No. 283)
55. Summary Report on the Status of the WMO Background Air Pollution Monitoring Network as at 31 December 1987 (TD No. 284)
56. Report of the First Session of the Executive Council Panel of Experts/CAS Working Group on Environmental Pollution and Atmospheric Chemistry, Hilo, Hawaii, 27-31 March 1988. June 1988
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58. Provisional Daily Atmospheric Carbon Dioxide Concentrations as measured at BAPMoN sites for the years 1986 and 1987 (TD No. 306)
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60. Global Atmospheric Background Monitoring for Selected Environmental Parameters. BAPMoN Data for 1984 and 1985, Volume II: Precipitation chemistry, continuous atmospheric carbon dioxide and suspended particulate matter.
61. Global Atmospheric Background Monitoring for Selected Environmental Parameters. BAPMoN Data for 1987 and 1988, Volume I: Atmospheric Aerosol Optical Depth.
62. Provisional Daily Atmospheric Carbon Dioxide Concentrations as measured at BAPMoN sites for the year 1988 (TD No. 355)
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69. Provisional Daily Atmospheric Carbon Dioxide Concentrations as measured at Global Atmosphere Watch (GAW)-BAPMoN sites for the year 1989 (TD No. 400)
70. Report of the Second Session of EC Panel of Experts/CAS Working Group on Environmental Pollution and Atmospheric Chemistry, Santiago, Chile, 9-15 January 1991 (TD No. 633)

71. Report of the Consultation of Experts to Consider Desirable Observational Practices and Distribution of GAW Regional Stations, Halkidiki, Greece, 9-13 April 1991 (TD No. 433)
72. Integrated Background Monitoring of Environmental Pollution in Mid-Latitude Eurasia by Yu.A. Izrael and F.Ya. Rovinsky, USSR (TD No. 434)
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74. Report of the Experts Meeting on Aerosol Physics and Chemistry, Hampton, Virginia, 30 to 31 May 1991 (TD No. 439)
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78. Global Atmospheric Background Monitoring for Selected Environmental Parameters BAPMoN Data for 1990, Volume I: Atmospheric Aerosol Optical Depth (TD No. 446)
79. Report of the Meeting of Experts to Consider the Aerosol Component of GAW, Boulder, 16 to 19 December 1991 (TD No. 485)
80. Report of the WMO Meeting of Experts on the Quality Assurance Plan for the GAW, Garmisch-Partenkirchen, Germany, 26-30 March 1992 (TD No. 513)
81. Report of the Second Meeting of Experts to Assess the Response to and Atmospheric Effects of the Kuwait Oil Fires, Geneva, Switzerland, 25-29 May 1992 (TD No. 512)
82. Global Atmospheric Background Monitoring for Selected Environmental Parameters BAPMoN Data for 1991, Volume I: Atmospheric Aerosol Optical Depth (TD No. 518)
83. Report on the Global Precipitation Chemistry Programme of BAPMoN (TD No. 526)
84. Provisional Daily Atmospheric Carbon Dioxide Concentrations as measured at GAW-BAPMoN sites for the year 1991 (TD No. 543)
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87. Report of the Third Session of EC Panel/CAS Working Group on Environmental Pollution and Atmospheric Chemistry, Geneva, 8-11 March 1993 (TD No. 555)
88. Report of the Seventh WMO Meeting of Experts on Carbon Dioxide Concentration and Isotopic Measurement Techniques, Rome, Italy, 7 - 10 September 1993, (edited by Graeme I. Pearman and James T. Peterson) (TD No. 669)
89. 4th International Conference on CO₂ (Carqueiranne, France, 13-17 September 1993) (TD No. 61)

90. Global Atmospheric Background Monitoring for Selected Environmental Parameters GAW Data for 1992, Volume I: Atmospheric Aerosol Optical Depth (TD No. 562)
91. Extended Abstracts of Papers Presented at the WMO Region VI Conference on the Measurement and Modelling of Atmospheric Composition Changes Including Pollution Transport, Sofia, 4 to 8 October 1993 (TD No. 563)
92. Report of the Second WMO Meeting of Experts on the Quality Assurance/Science Activity Centres of the Global Atmosphere Watch, Garmisch-Partenkirchen, 7-11 December 1992 (TD No. 580)
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94. Report on the Measurements of Atmospheric Turbidity in BAPMoN (TD No. 603)
95. Report of the WMO Meeting of Experts on UV-B Measurements, Data Quality and Standardization of UV Indices, Les Diablerets, Switzerland, 25-28 July 1994 (TD No. 625)
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97. Quality Assurance Project Plan (QAPjP) for Continuous Ground Based Ozone Measurements (TD No. 634)
98. Report of the WMO Meeting of Experts on Global Carbon Monoxide Measurements, Boulder, USA, 7-11 February 1994 (TD No. 645)
99. Status of the WMO Global Atmosphere Watch Programme as at 31 December 1993 (TD No. 636)
100. Report of the Workshop on UV-B for the Americas, Buenos Aires, Argentina, 22-26 August 1994
101. Report of the WMO Workshop on the Measurement of Atmospheric Optical Depth and Turbidity, Silver Spring, USA, 6-10 December 1993, (edited by Bruce Hicks) (TD No. 659)
102. Report of the Workshop on Precipitation Chemistry Laboratory Techniques, Hradec Kralove, Czech Republic, 17-21 October 1994 (TD No. 658)
103. Report of the Meeting of Experts on the WMO World Data Centres, Toronto, Canada, 17-18 February 1995, (prepared by Edward Hare) (TD No. 679)
104. Report of the Fourth WMO Meeting of Experts on the Quality Assurance/Science Activity Centres (QA/SACs) of the Global Atmosphere Watch, jointly held with the First Meeting of the Coordinating Committees of IGAC-GLONET and IGAC-ACE, Garmisch-Partenkirchen, Germany, 13 to 17 March 1995 (TD No. 689)
105. Report of the Fourth Session of the EC Panel of Experts/CAS Working Group on Environmental Pollution and Atmospheric Chemistry (Garmisch, Germany, 6-11 March 1995) (TD No. 718)
106. Report of the Global Acid Deposition Assessment (edited by D.M. Whelpdale and M-S. Kaiser) (TD No. 777)

107. Extended Abstracts of Papers Presented at the WMO-IGAC Conference on the Measurement and Assessment of Atmospheric Composition Change (Beijing, China, 9-14 October 1995) (TD No. 710)
108. Report of the Tenth WMO International Comparison of Dobson Spectrophotometers (Arosa, Switzerland, 24 July - 4 August 1995)
109. Report of an Expert Consultation on ⁸⁵Kr and ²²²Rn: Measurements, Effects and Applications (Freiburg, Germany, 28-31 March 1995) (TD No. 733)
110. Report of the WMO-NOAA Expert Meeting on GAW Data Acquisition and Archiving (Asheville, NC, USA, 4-8 November 1995) (TD No. 755)
111. Report of the WMO-BMBF Workshop on VOC Establishment of a "World Calibration/Instrument Intercomparison Facility for VOC" to Serve the WMO Global Atmosphere Watch (GAW) Programme (Garmisch-Partenkirchen, Germany, 17-21 December 1995) (TD No. 756)
112. Report of the WMO/STUK Intercomparison of Erythemally-Weighted Solar UV Radiometers, Spring/Summer 1995, Helsinki, Finland (TD No. 781)
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114. Report of the Fifth WMO Meeting of Experts on the Quality Assurance/Science Activity Centres (QA/SACs) of the Global Atmosphere Watch, jointly held with the Second Meeting of the Coordinating Committees of IGAC-GLONET and IGAC-ACE^{Ed}, Garmisch-Partenkirchen, Germany, 15-19 July 1996 (TD No. 787)
115. Report of the Meeting of Experts on Atmospheric Urban Pollution and the Role of NMSs (Geneva, 7-11 October 1996) (TD No. 801)
116. Expert Meeting on Chemistry of Aerosols, Clouds and Atmospheric Precipitation in the Former USSR (Sankt Peterburg, Russian Federation, 13-15 November 1995)
117. Report and Proceedings of the Workshop on the Assessment of EMEP Activities Concerning Heavy Metals and Persistent Organic Pollutants and their Further Development (Moscow, Russian Federation, 24-26 September 1996) (Volumes I and II) (TD No. 806)
118. Report of the International Workshops on Ozone Observation in Asia and the Pacific Region (IWOAP, IWOAP-II), (IWOAP, 27 February-26 March 1996 and IWOAP-II, 20 August-18 September 1996) (TD No. 827)
119. Report on BoM/NOAA/WMO International Comparison of the Dobson Spectrophotometers (Perth Airport, Perth, Australia, 3-14 February 1997), (prepared by Robert Evans and James Easson) (TD No. 828)
120. WMO-UMAP Workshop on Broad-Band UV Radiometers (Garmisch-Partenkirchen, Germany, 22 to 23 April 1996) (TD No. 894)
121. Report of the Eighth WMO Meeting of Experts on Carbon Dioxide Concentration and Isotopic Measurement Techniques (prepared by Thomas Conway) (Boulder, CO, 6-11 July 1995) (TD No. 821)
122. Report of Passive Samplers for Atmospheric Chemistry Measurements and their Role in GAW (prepared by Greg Carmichael) (TD No. 829)

123. Report of WMO Meeting of Experts on GAW Regional Network in RA VI, Budapest, Hungary, 5 to 9 May 1997
124. Fifth Session of the EC Panel of Experts/CAS Working Group on Environmental Pollution and Atmospheric Chemistry, (Geneva, Switzerland, 7-10 April 1997) (TD No. 898)
125. Instruments to Measure Solar Ultraviolet Radiation, Part 1: Spectral Instruments (lead author G. Seckmeyer) (TD No. 1066)
126. Guidelines for Site Quality Control of UV Monitoring (lead author A.R. Webb) (TD No. 884)
127. Report of the WMO-WHO Meeting of Experts on Standardization of UV Indices and their Dissemination to the Public (Les Diablerets, Switzerland, 21-25 July 1997) (TD No. 921)
128. The Fourth Biennial WMO Consultation on Brewer Ozone and UV Spectrophotometer Operation, Calibration and Data Reporting, (Rome, Italy, 22-25 September 1996) (TD No. 918)
129. Guidelines for Atmospheric Trace Gas Data Management (Ken Masarie and Pieter Tans), 1998 (TD No. 907)
130. Jülich Ozone Sonde Intercomparison Experiment (JOSIE, 5 February to 8 March 1996), (H.G.J. Smit and D. Kley) (TD No. 926)
131. WMO Workshop on Regional Transboundary Smoke and Haze in Southeast Asia (Singapore, 2 to 5 June 1998) (Gregory R. Carmichael). Two volumes
132. Report of the Ninth WMO Meeting of Experts on Carbon Dioxide Concentration and Related Tracer Measurement Techniques (Edited by Roger Francey), (Aspendale, Vic., Australia)
133. Workshop on Advanced Statistical Methods and their Application to Air Quality Data Sets (Helsinki, 14-18 September 1998) (TD No.956)
134. Guide on Sampling and Analysis Techniques for Chemical Constituents and Physical Properties in Air and Precipitation as Applied at Stations of the Global Atmosphere Watch. Carbon Dioxide
135. Sixth Session of the EC Panel of Experts/CAS Working Group on Environmental Pollution and Atmospheric Chemistry (Zurich, Switzerland, 8-11 March 1999) (WMO TD No.1002)
136. WMO/EMEP/UNEP Workshop on Modelling of Atmospheric Transport and Deposition of Persistent Organic Pollutants and Heavy Metals (Geneva, Switzerland, 16-19 November 1999) (Volumes I and II) (TD No. 1008)
137. Report and Proceedings of the WMO RA II/RA V GAW Workshop on Urban Environment (Beijing, China, 1-4 November 1999) (WMO-TD. 1014) (Prepared by Greg Carmichael)
138. Reports on WMO International Comparisons of Dobson Spectrophotometers, Parts I – Arosa, Switzerland, 19-31 July 1999, Part II – Buenos Aires, Argentina (29 Nov. – 12 Dec. 1999 and Part III – Pretoria, South Africa (18 March – 10 April 2000).
139. The Fifth Biennial WMO Consultation on Brewer Ozone and UV Spectrophotometer Operation, Calibration and Data Reporting (Halkidiki, Greece, September 1998)(WMO TD No. 1019).
140. WMO/CEOS Report on a Strategy for Integrating Satellite and Ground-based Observations of Ozone (WMO TD No. 1046).

141. Report of the LAP/COST/WMO Intercomparison of Erythral Radiometers (Thessaloniki, Greece, 13-23 September 1999) (WMO TD No. 1051).
142. Strategy for the Implementation of the Global Atmosphere Watch Programme (2001-2007), A Contribution to the Implementation of the Long-Term Plan (WMO TD No.1077)
143. Global Atmosphere Watch Measurements Guide (WMO TD No. 1073)
144. Report of the Seventh Session of the EC Panel of Experts/CAS Working Group on Environmental Pollution and Atmospheric Chemistry and the GAW 2001 Workshop (Geneva, Switzerland, 2 to 5 April 2001)
145. WMO GAW International Comparisons of Dobson Spectrophotometers at the Meteorological Observatory Hohenpeissenberg, Germany (21 May – 10 June 2000, MOHp2000-1), 23 July – 5 August 2000, MOHp2000-2), (10 – 23 June 2001, MOHp2001-1) and (8 to 21 July 2001, MOHp2001-2). Prepared by Ulf Köhler (WMO TD No. 1114).
146. Quality Assurance in monitoring solar ultraviolet radiation: the state of the art. (not yet published)
147. Workshop on GAW in RA VI (Europe), Riga, Latvia, 27-30 May 2002 (not yet published)
148. Report of the Eleventh WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracer Measurement Techniques (Tokyo, Japan, 25-28 September 2001) (WMO TD No 1138)
149. Comparison of Total Ozone Measurements of Dobson and Brewer Spectrophotometers and Recommended Transfer Functions (prepared by J. Staehelin, J. Kerr, R. Evans and K. Vanicek) WMO TD No. 1147
150. Updated Guidelines for Atmospheric Trace Gas Data Management (Prepared by Ken Maserie and Pieter Tans)
151. Report of the First CAS Working Group on Environmental Pollution and Atmospheric Chemistry (Geneva, Switzerland, 18-19 March 2003)
152. Current Activities of the Global Atmosphere Watch Programme (as presented at the 14th World Meteorological Congress, May 2003). WMO TD No. 1168
153. WMO/GAW Aerosol Measurement Procedures: Guidelines and Recommendations. TD No. 1178.