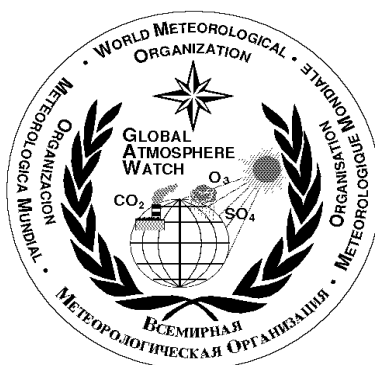


WORLD METEOROLOGICAL ORGANIZATION GLOBAL ATMOSPHERE WATCH



No. 143

GLOBAL ATMOSPHERE WATCH MEASUREMENTS GUIDE



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1. INTRODUCTION

The WMO's Global Atmosphere Watch (GAW) integrates many monitoring and research activities involving the measurement of the chemical and physical properties of the atmosphere. GAW serves as an early warning system to detect further changes in atmospheric concentrations including acidity and toxicity of rain as well as atmospheric burden of aerosols. This system, approved in June 1989 by the WMO Executive Council, will provide framework design, standards, intercalibrations, and data collection systems for global monitoring and data evaluation.

The following is a short overview of the GAW programme:

Objective To monitor the long-term evolution of the atmospheric composition on a global and regional scale in order to assess this contribution to climate change and environmental issues.

Major Goals To co-ordinate and assess atmospheric chemistry measurements and associated physical parameters in relation to climate change (greenhouse gases, ozone and aerosols).

To evaluate the influence of atmospheric chemistry on the environment including transboundary and urban pollution (air quality, acid deposition, stratospheric ozone depletion and increasing UV radiation).

Parameters Greenhouse gases (carbon dioxide, CFCs, methane, nitrous oxide, tropospheric ozone)

Ozone (surface, total column, vertical profile by both ground-based and satellite)

Solar radiation including ultraviolet

Precipitation chemistry

Chemical and physical properties of aerosols including optical depth

Reactive gases (carbon monoxide, sulfur dioxide, nitrogen oxides, volatile organic compounds)

Persistent organic pollutants and heavy metals

Radionuclides (krypton-85, radon-222, beryllium-7, lead-210)

Meteorological parameters

Network GAW *Global* stations: 22 stations that are usually situated in remote locations, have very low background levels of pollutants that are representative of large geographic areas, and continuously measure a broad range of atmospheric parameters over decades; typically related to climate change and stratospheric ozone depletion.

GAW *Regional* stations: about 400 stations representing smaller geographic regions that are not affected by nearby sources of pollution such as vehicular and industrial combustion or agricultural activities; data are typically applied to more regional issues such as acid deposition, transport of trace gases and aerosols, and local UV radiation.

Contributing and *Associate* stations co-operate with GAW and submit data to the World Data Centres.

- Modelling** Support atmospheric modelling of transboundary transport of pollutants, UV modelling/UV Index calculations and urban pollution transport.
- Satellite** Close co-operation with satellite programmes measuring trace components, especially ozone and aerosols.
- Activities** The GAW programme is implemented through:
 Technical meetings, workshops and conferences
 Publications, data collection and assessments
 Training and technology transfer especially for developing countries
 Quality assurance activities - instrument calibrations/intercomparisons
 Twinning partnerships.
- Supporting Structure**
 WMO Members
 WMO Secretariat
 Scientific Advisory Groups (SAG) for
 Aerosols
 Greenhouse gases
 Ozone
 Precipitation chemistry
 UV Radiation
 GAW Urban Research Meteorology and Environment Project (GURME)
 Quality Assurance Science Activity Centres (QA/SAC)
 QA/SAC Germany
 QA/SAC Switzerland
 QA/ SAC USA
 QA/SAC Japan
 GAW World Calibration Centres
 Centres established for carbon dioxide, total column ozone, surface ozone, vertical ozone, solar radiation, precipitation chemistry, carbon monoxide, aerosols, optical depth, radioactivity
 WMO World Data Centres (WDC)
 Aerosols (WDCA) in Ispra, Italy (EU)
 Greenhouse gases and other trace gases (WDCGG) in Japan
 Precipitation Chemistry (WDCPC) in the USA
 Solar Radiation (WRDC) in Russia
 Surface Ozone (WDCSO) in Norway
 UV Radiation and Ozone (WOUDC) in Canada
 WMO GAW Ozone Mapping Centre (WO₃DC) in Greece
- Planning** A Strategy for the Implementation of the GAW through the year 2007 is being implemented.

The following Guide provides short overviews of selected GAW measurement parameters as a quick reference source for administrators and scientists.

2. GASES

2.1 Greenhouse Gases

2. 1. 1. Carbon Dioxide

Importance

Carbon Dioxide (CO₂) is one of the most common and important trace gases in the earth-ocean-atmosphere system. It has both natural and anthropogenic sources. Within the natural carbon cycle, CO₂ plays a key role in a number of biological processes. Coal, oil, natural gas, and wood are mostly carbon, so combustion of these fuels releases CO₂ into the atmosphere, and this has been the cause of the continuous increase in atmospheric CO₂ abundance over the last several decades. Because of CO₂'s role as one of the more important greenhouse gases, scientists have attempted to understand its potential impact on climate and global change.

Site Requirements

Atmospheric CO₂ is one of the required measurements made at global sites under the GAW programme. The purpose is to monitor its rising atmospheric abundance and its potential as a greenhouse gas, and to evaluate its role in the global carbon cycle. Because of its long residence in the atmosphere, a background level can be determined and has been documented at such sites as Mauna Loa, Hawaii; Cape Grim, Australia; and other global sites. At regional sites, where a number of sources and sinks (mainly vegetation) are present, it is more difficult to find a clear global signal. However, these sites are useful in quantifying the processes by which the gas is exchanged in the environment.

Methods of Measurement and Sampling Frequency

At present, most background atmospheric CO₂ measurements are made with Non-Dispersive Infra-Red (NDIR) gas analysers, but a few programmes use a gas chromatographic (GC) method. The GC method requires separation of CO₂ from other gases in the air sample, reduction of this CO₂ over a catalyst with H₂ to CH₄, and detection of the CO₂-derived CH₄ by flame ionisation detector (FID). Chromatographic peak responses from samples are compared to those from standards with known CO₂ mole fractions to calculate the CO₂ mole fraction in the sample. GC techniques are limited to a measurement frequency of 1 sample every few minutes. NDIR instruments are based on the same principle that makes CO₂ a greenhouse gas: its ability to absorb IR radiation. NDIRs measure the intensity of IR radiation passing through a "sample" cell relative to radiation passing through a reference cell. It is not necessary to know the CO₂ mole fraction of the reference cell gas. Sample air, pumped from inlets mounted well-away from the measurement building, and standard gas flow alternately through the sample cell. A difference in CO₂ concentration between sample and reference gases (or standard and reference gases) contained in the two cells results in a voltage that is recorded by the data acquisition system.

Carbon dioxide abundances are reported in dry-air mole fraction, $\mu\text{mol mol}^{-1}$, abbreviated ppm, on the WMO CO₂ Mole Fraction scale (see below QA/QC). Samples must be dried for two reasons: 1. H₂O also absorbs IR radiation and can interfere with the measurement of CO₂; 2. H₂O occupies volume in the sample cell. At warm, humid sites, 3% of the total volume of air can be H₂O vapour. Drying to a dewpoint of -50°C is sufficient.

To obtain global intercomparability of background CO₂ measurements, a calibration system has been developed that uses a hierarchy of standards, consisting of at least secondary, and working standards, but usually with three levels of standards. Secondary standards should be calibrated once every two years vs the primary standards maintained at the Central CO₂ calibration Laboratory ("CCL", NOAA Climate Monitoring and Diagnostics Laboratory, USA).

The NDIR gives a constant trace of the ambient CO₂ mole fraction, broken at set intervals with standard gas measurements. At least once a week, a calibration test is made using higher-level standards. A GC method gives a measurement frequency of one sample every few minutes.

An alternate method of CO₂ measurement that is generally applicable to many other trace gases is collection of discrete air samples in vacuum-tight flasks. These flasks are returned to a central laboratory where CO₂ is determined by NDIR or GC. This method is used where low-frequency sampling (e.g., once a week) is adequate to define CO₂ spatial and temporal gradients, and for comparison with in situ measurements as a quality control step. This sampling strategy has the advantage that many species can be determined from the same sample.

QA/QC

Many activities are required to insure high-quality CO₂ data. At the highest level, these activities include maintaining a standard scale that is traceable to the WMO CO₂ mole fraction scale and frequent scientific scrutiny of the data. A direct link of standards to the WMO scale is maintained by having standards calibrated once every two years. Regular scientific scrutiny of the data can only occur if a reasonable database management system and graphics capability to view data in near-real-time are in place. Spread sheets are not an adequate data base management system (see WMO/GAW Report No. 129, "Guidelines for Atmospheric Trace Gas Data Management").

Quality control can also be insured by scrutinizing recorded instrument parameters such as pressure and flow rate. This can be done manually or with software.

It is essential for measurement programmes to have redundancy built into them. When inconsistencies appear among duplicate measurements, then the search for the cause can start. Some examples of precautionary measures are:

1. Carefully collect discrete samples that can be compared with in situ measurements. Normally analyse at a central laboratory that also maintains a programme's highest level standards.
2. Routinely analyse air from a "surveillance" cylinder as part of an in situ measurement programme, (e.g., randomly once per day).
3. For in situ operations, use two different intake lines. If one line has a leak inside the observatory building, it will be obvious.
4. Analyse "test" samples from flasks that were filled from a cylinder of natural air. These test flasks should be analysed every day that discrete samples are analysed.

There is no universal scheme to insure high-quality data; each programme should develop a scheme, with guidance from other successful programmes, suitable to their own needs.

Ancillary measurements

The most important ancillary measurements are meteorological data including wind speed and direction, temperature, dewpoint, and pressure.

Archiving Procedures

CO₂ data are archived at the Carbon Dioxide Information and Analysis Centre in Oak Ridge, USA, and since 1990, with the WMO World Data Centre for Greenhouse Gases, operated by the Japan Meteorological Agency in Tokyo.

Data Treatment

NDIR voltages for modern instruments are recorded on an electronic data acquisition system; a chart recorder may be used as backup. The voltages measured from standards (i.e., the

period of calibration) characterize the instrument response curve, which is then used to calculate time-averaged CO₂ mole fractions (e.g., 1 minute averages). If possible, data obtained when the sampling and analytical system are working less than optimally are identified and excluded from further analysis. To separate periods of local influence on CO₂ from background conditions, data are “selected” based on conditions unique to each measurement site. These selected data are used in subsequent studies. Data with local influences are never deleted, but are “flagged” in the database. These data may be used for local- to regional-scale studies.

Application of Results

The CO₂ data have been used extensively by the scientific community to investigate carbon cycle processes such as exchange between the atmosphere and the ocean or uptake of carbon by the biosphere, and to predict the long-range climate effects of increasing CO₂ abundance.

Equipment and Infrastructure Cost (US \$)

CO₂ In-Situ Analyser - Remote Global Station

Analyser - 8,000 to 18,000 depending on model (one-time cost)
Standard gases - 12,000 for 6 cylinders (one-time cost)
Plumbing hardware - 6,000 (one-time cost)
Data Acquisition - 8,000 (one-time cost)
Standards recalibration - 2,000 (annual cost)
*Working standards - 8,000 (annual cost)

Total Start-up Cost: 42,000 to 52,000

*Working standards can be prepared by programme to save money, but requires large initial start-up cost.

Note: Software for instrument control, database management, and data analysis are not included in the cost estimates, and can be up to \$10,000 extra.

CO₂ Flask Sampling at Remote Sites

Flasks (40) and sampler for one site - 11,000 + shipping costs
Central Analysis Lab - 32,000 to 42,000
Calibration Facility - 40,000 to 50,000

Personnel Requirements and Training

Personnel: NDIR operator at global - 8 man-months per year
Central Laboratory - 18 man-months per year
(Depending on number of sites and sampling frequency)

Training: NDIR operator for global location or Central Laboratory - 2 months
Discrete sample collection - 2 days

References

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2.1.2. Methane

Importance

Methane (CH₄) is a strong greenhouse gas, and it plays important roles in determining the oxidizing capacity of the troposphere and in stratospheric ozone depletion. The atmospheric burden of methane CH₄ in the late 1990s is $\sim 4800 \times 10^{12}$ g, more than twice the amount present during the pre industrial era. This doubling in CH₄ burden contributes $\sim 20\%$ of the direct radiative forcing due to anthropogenic greenhouse gas emissions. Though this increase is clearly linked to human activities, a quantitative understanding of the methane budget (sources and sinks) has not yet been achieved. This understanding is necessary if reasonable policies are to be developed to mitigate the potential influence of CH₄ on climate.

Site Requirements

The distribution of methane in the remote tropospheric boundary layer, particularly in the high latitudes of the southern hemisphere, is fairly well established. There are still many regions with strong CH₄ sources that are poorly characterized, including populated regions of the mid-latitudes of the northern hemisphere, agricultural regions in South and Southeast Asia, and vast regions of the Russian Arctic, where natural wetlands and fossil fuel exploitation result in significant emissions. To provide better constraints on model syntheses of the global methane budget, more measurements of CH₄ vertical profiles are also clearly needed.

Measurement Methods and Sampling Frequency

Almost all measurements of CH₄ used in background monitoring are made by gas chromatography (GC) with flame ionization detection (FID). These GC systems are reliable and less difficult to operate and maintain than optical measurement systems. Various chromatographic schemes are employed. The goal of the chromatographic method is to insure good separation of CH₄ from air (N₂ + O₂) and other constituents, and also to insure that compounds with long elution times are backflushed or given sufficient time to elute before the next run is started. Laboratories planning to begin CH₄ measurements should consult the literature or well-established programmes to determine which method would best fits their needs.

There are no absolute measurement methods with sufficient precision to meet the scientific requirements of background CH₄ monitoring. Therefore all CH₄ measurements are made relative to standard gases, and each laboratory monitoring atmospheric CH₄ should realize that, in addition to maintaining their analytical instruments, they must also maintain a hierarchy of CH₄ standards. These standards are typically dry (<10 ppm H₂O vapour) natural air contained in high-pressure cylinders. Primary and working standards can initially be purchased, but, to insure internal consistency in a measurement record, as standards are depleted, it is necessary to propagate the primary standard scale to new working standards.

An internationally accepted CH₄ standard scale does not exist; each laboratory maintains its own set of “primary” and working standards. Since significant differences exist between different scales, it is critical that programmes involved in CH₄ monitoring frequently intercalibrate so maximum benefit can be made of measurements.

Two sampling strategies are typically used: discrete and continuous. Discrete samples are collected in a suitable container and shipped to a central laboratory where they are analyzed for CH₄. The major advantages of this strategy are that multiple species can be determined from each sample and all measurements are made for a given species on the same analyzer relative to the same standards. The major disadvantage is that data records are relatively low frequency. In situ measurements involve continuously drawing air from a suitable intake and periodically injecting aliquots of air for analysis. Typical sampling frequencies for CH₄ are 2 to 4 aliquots of air per hour, alternating with an equal number of aliquots of standard. It is critical for both methods that sampling does not affect the composition of the air. Preferably, analytical systems used with both sampling strategies are automated.

QA/QC

Many activities are required to insure high-quality CH₄ data. At the highest level, these activities include maintaining an internally-consistent standard gas scale and frequent scientific scrutiny of the data. Regular scientific scrutiny of the data can occur only if a reasonable data base management system and graphics capability to view data in near-real-time are available. Experts should regularly examine plots of the data to insure the values are reasonable, and to begin searching for the reasons if they are not.

Quality control can also be enhanced by scrutinizing “engineering data” recorded from an analysis system such as pressures, temperatures, and flow rates. With chromatographic methods, additional QC information is available from chromatographic parameters that include peak retention time and peak width.

It is essential for measurement programmes to have redundancy built into them. When inconsistencies appear among duplicate measurements, then the search for the cause can start. Some examples of precautionary measures are:

1. Carefully collect discrete samples that can be compared with in situ measurements. Normally analyse at a central laboratory that also maintains a programme’s highest level standards.
2. Routinely analyse air from a “surveillance” cylinder as part of an in situ measurement programme, (e.g., randomly once per day).
3. For *in situ* operations, use two different intake lines. If one intake has a leak inside the observatory building, it will be obvious when the results from the two lines are compared.
4. Analyse “test” samples from flasks that were filled from a cylinder of natural air. Test flasks should be analysed every day that discrete samples are analysed.
5. Share samples with other measurement programmes and routinely compare results.

There is no universal scheme to insure high-quality data; each programme should develop a scheme, with guidance from other successful programmes, suitable to their own needs.

Ancillary Measurements

The most important ancillary measurements are meteorological data including wind speed and direction, temperature, dewpoint, and pressure.

Archiving Procedures

Data from GAW sites are archived with the WMO World Data Centre for Greenhouse Gases (WDCGG), operated by the Japan Meteorological Agency in Tokyo. Many programmes

Data Treatment

Application of Results

Equipment Infrastructure and Cost (US\$)

Gas Chromatograph	17,000 (one-time cost)
Data Acquisition	7,000 (Hardware only - one-time cost)
Plumbing Hardware	5,000 (one-time cost)
Gases and Expendables	10,000 (annual cost)
Standards	2,000 (annual cost)
Total Start-up Cost	41,000 (includes one year of operation)

Flasks and Sampler	7,000 (per site) + shipping costs
Central Analytical Lab	60,000 (start-up + 1 year operation)

Personnel Requirements and Training

Training: GC Operator – 3 months (operator needs prior analytical experience)
Sample collector – 2 days (conscientious attitude required)

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2.1.3. Chlorofluorocarbons

Importance

Chlorofluorocarbons (CFCs), which include CFC-11 (CFCl_3) and CFC-12 (CF_2Cl_2), are a family of compounds that do not naturally exist in the environment. Since manufacture began in the 1930s, CFCs have been used as refrigerant gases, as solvents in industrial applications and dry cleaning, and as propellant in aerosol cans. CFCs are unreactive in the troposphere, but in the stratosphere they are photolyzed to release chlorine atoms that catalytically destroy ozone. They also contribute to the enhanced greenhouse effect. Production of both compounds has been banned by the Montreal Protocol and its amendments; as a result, the abundance CFC-11 at Earth's surface has started to decrease and the rate of increase CFC-12 has declined significantly, though it still continues to accumulate in the atmosphere.

Site Requirements

CFCs are measured on a routine basis at some of the GAW global stations. Because of their long residence time, background levels can be readily obtained in the remote troposphere. At regional stations, however, local sources may interfere with obtaining a representative background signal, but these measurements can be used to define regional emission estimates.

Methods of Measurement and Sampling Frequency

The standard technique to measure CFCs is gas chromatography on site. After drying, an aliquot of air is injected into a gas chromatograph, the compounds of interest are separated on an appropriate column, and they are quantified with an electron capture detector. The units of measurement are dry-air mole fraction (pmol mol^{-1} for background conditions, usually abbreviated ppt). Calibration gas measurements are interspersed with air sample measurements to obtain absolute mole fractions.

An alternative to on-site determination is to collect samples in clean, stainless steel flasks and return them to a central laboratory for analysis.

QA/QC

Many activities are required to insure high-quality data. At the highest level, these activities include maintaining an internally-consistent standard gas scale and frequent scientific scrutiny of the data. Regular scientific scrutiny of the data can only occur if a reasonable database management system and graphics capability to view data in near-real-time are in place. Experts should regularly examine plots of the data to insure the values are reasonable, and to begin searching for the reasons if they are not.

Quality control can also be enhanced by scrutinizing “engineering data” recorded from an analysis system such as pressures, temperatures, and flow rates. With chromatographic methods, additional QC information is available from chromatographic parameters that include peak retention time and peak width.

It is essential for measurement programmes to have redundancy built into them. When inconsistencies appear among duplicate measurements, then the search for the cause can start. Some examples of precautionary measures are:

1. Carefully collect discrete samples that can be compared with in situ measurements. Normally analyse at a central laboratory that also maintains a programme’s highest level standards.
2. Routinely analyse air from a “surveillance” cylinder as part of an in situ measurement programme, (e.g., randomly once per day).
3. For in situ operations, use two different intake lines. If one intake has a leak inside the observatory building, it will be obvious.
4. Analyse “test” samples from flasks that were filled from a cylinder of natural air. These test flasks should be analysed every day that discrete samples are analysed.
5. Share samples with other measurement programmes and routinely compare results.

There is no universal scheme to insure high-quality data; each programme should develop a scheme, with guidance from other successful programmes, suitable to their own needs.

Ancillary measurements

The most important ancillary measurements are meteorological data including wind speed and direction, temperature, dewpoint, and pressure.

Archiving Procedures

CFC data are archived at the Carbon Dioxide Information and Analysis Centre in Oak Ridge, USA, and since 1990, with the WMO World Data Centre for Greenhouse Gases, operated by the Japan Meteorological Agency in Tokyo.

Data Treatment

Chromatograms are recorded by an integrator or computer which determines peak heights and areas. Mixing ratios for the samples are determined relative to the standard. The data are edited for periods when the instrument was not operating optimally and for periods when their levels do not reflect background conditions.

Application of Results

Data obtained from the CFC monitoring programmes are used both in climate and stratospheric ozone depletion studies. Also, validation of reported industrial emissions, source and sink estimates, and lifetime calculations depend on CFC measurements.

Equipment Infrastructure and Cost (US \$)

In-Situ CFC Analytical System

Gas Chromatograph	20,000 (one-time cost)
Data Acquisition	7,000 (Hardware only - one-time cost)
Plumbing Hardware	5,000 (one-time cost)
Gases and Expendables	10,000 (annual cost)
Standards	2,000 (annual cost)
Total Start-up Cost	44,000 (includes one year of operation)

CFC Discrete Sampling at Remote Site

Stainless Steel Flasks (12) and sampler - 10,000 + shipping costs
Central Laboratory - 44,000

Personnel Requirements and Training

Personnel: In-situ system - 5 hours per week (weekly maintenance)
- 2 weeks per year (yearly maintenance)

Central Laboratory - 1 full-time staff

Training: GC operator - 3 months
Sample taker - 3 days

References

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2.1.4. Nitrous Oxide

Importance

Nitrous oxide (N₂O) has both natural and anthropogenic sources and contributes about 6% to the enhanced greenhouse effect. It is increasing at about 0.7 ppb yr⁻¹. Sources include the oceans, fossil fuel combustion, biomass burning, and agriculture. Nitrous oxide is inert in the troposphere. Its major sink is through photochemical transformations in the stratosphere that affect the abundance of stratospheric ozone.

Site Requirements

Because of its long atmospheric lifetime (150 years), background levels of nitrous oxide can be determined at GAW global stations. Local sources can interfere with measurements at regional sites.

Methods of Measurement and Sampling Frequency

Like the CFCs, N₂O is measured on site by GC with electron capture detection. N₂O mole fractions are determined by comparing the chromatographic peak responses from aliquots of sample gas with those from standard gases of known N₂O mole fraction. The units of measurement are dry-air mole fraction (nmol mol⁻¹ for background conditions, usually abbreviated ppb).

Discrete sampling of N₂O is an alternative method of monitoring its abundance. Flasks containing air samples are returned to a central laboratory for analysis.

QA/QC

Many activities are required to insure high-quality N₂O data. At the highest level, these activities include maintaining an internally-consistent standard gas scale and frequent scientific scrutiny of the data. Regular scientific scrutiny of the data can only occur if a reasonable data base management system and graphics capability to view data in near-real-time are in place. Experts should regularly examine plots of the data to insure the values are reasonable, and to begin searching for the reasons if they are not.

Quality control can also be enhanced by scrutinizing “engineering data” recorded from an analysis system such as pressures, temperatures, and flow rates. With chromatographic methods, additional QC information is available from chromatographic parameters that include peak retention time and peak width.

It is essential for measurement programmes to have redundancy built into them. When inconsistencies appear among duplicate measurements, then the search for the cause can start. Some examples of precautionary measures are:

1. Carefully collect discrete samples that can be compared with in situ measurements. Normally analyse at a central laboratory that also maintains a programme's highest level standards.
2. Routinely analyse air from a “surveillance” cylinder as part of an in situ measurement programme, (e.g., randomly once per day).
3. For in situ operations, use two different intake lines. If one intake has a leak inside the observatory building, it will be obvious.
4. Analyse “test” samples from flasks that were filled from a cylinder of natural air. These test flasks should be analysed every day that discrete samples are analysed.
5. Share samples with other measurement programmes and routinely compare results.

There is no universal scheme to insure high-quality data; each programme should develop a scheme, with guidance from other successful programmes, suitable to their own needs.

Ancillary measurements

The most important ancillary measurements are meteorological data including wind speed and direction, temperature, dewpoint, and pressure.

Archiving Procedures

N₂O data are archived at the Carbon Dioxide Information and Analysis Centre in Oak Ridge, USA, and since 1990, with the WMO World Data Centre for Greenhouse Gases, operated by the Japan Meteorological Agency in Tokyo.

Data Treatment

Chromatograms are recorded by an integrator or computer that determines peak heights and areas. Mixing ratios for the samples are determined relative to the standard. The data are edited for periods when the instrument was not operating optimally and for periods when the measurements do not reflect background conditions.

Application of Results

N₂O observations are used to quantify trends for climate models and stratospheric ozone studies, and to determine spatial distributions that are used to define the global budget of N₂O sources and sinks.

Equipment and Infrastructure Cost (US \$)

In situ N₂O Analytical System

Gas Chromatograph	20,000 (one-time cost)
Data Acquisition	7,000 (Hardware only - one-time cost)
Plumbing Hardware	5,000 (one-time cost)
Gases and Expendables	10,000 (annual cost)
Standards	2,000 (annual cost)
Total Start-up Cost	44,000 (includes one year of operation)

Note: Much of the system hardware can be shared with other GC measurement systems decreasing the cost of adding additional measurements.

N₂O Discrete Sampling at Remote Site

Stainless Steel Flasks (12) and sampler - 10,000 + shipping costs
Central Laboratory - 44,000

Personnel Requirements and Training

Personnel: In-situ system - 5 hours per week (weekly maintenance)
- 2 weeks per year (yearly maintenance)

Training: GC operator - 3 months
Sample taker - 2 days

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2.2 Ozone

2.2.1. Total Column Ozone

Importance

Atmospheric ozone is unevenly distributed vertically with about 90% of its mass in the stratosphere. During the last few decades, understanding man's impact on the amount overhead (total column) and the vertical distribution of atmospheric ozone has been a major environmental challenge. It is now well established that man is responsible for much of the observed decrease in total column ozone that was first reported over the Antarctic in 1985, but is now found also over the Arctic and at mid-latitudes.

In the stratosphere, ozone is an important absorber of UV radiation. It shields the biosphere from excessive UV at ground level, where it has adverse effects on biological systems. Because of these environmental impacts, the Montreal Protocol and its subsequent amendments were negotiated during the past two decades to reduce CFCs and other gases that cause destruction of ozone in the stratosphere.

By absorption of the solar UV radiation ozone also influences thermodynamical processes in the atmosphere and consequently large-scale circulation patterns, mainly in the lower stratosphere. In this way ozone represents an important factor in climate change.

Siting Requirements

Total column ozone was measured at only a few sites from the late 1920s until the International Geophysical Year (1958). Since then systematic monitoring has been carried out at many locations around the globe. These measurements, formerly performed under the Global Ozone Observing System, have been coordinated within the WMO GAW programme and the data are recorded in the World Ozone and Ultraviolet Data Centre (WOUDC) in Toronto, Canada. A major factor in site selection for column ozone is a frequent cloud-free view of the sun throughout the year and low concentration of air pollutants. Appropriate housing for the instrument is essential in order to minimise temperature fluctuations of the instrument which cause problems in maintaining the extremely high $\pm 1\%$ measurement accuracy required. It is also essential that trained observers be available daily for frequent measurements whenever the clear sky conditions are present since observations are usually performed with manually operated instruments.

Methods of Measurement and Sampling Frequency

Three major types of instruments are currently used for ground-based measurement of total ozone. All of them use the principle of different absorption of solar UV radiation by ozone at different wavelengths. The UV wavelengths are chosen in pairs between 290 and 340 nm with one wavelength strongly absorbed by ozone and the other not.

The Dobson Spectrophotometer was developed in the early 1920s by G.M.B. Dobson, and has been the backbone of the total ozone measuring network. The instruments presently used are double monochromators which compare solar UV intensity at a few fixed pairs of wavelengths. One wavelength is chosen to absorb ozone strongly, and the other of the pair somewhat less. From instrument calibration factors, previous knowledge of the ozone absorption cross-sections, and geometric factors related to the position of the sun, the total column ozone is calculated.

The Brewer Grating Spectrophotometer uses a diffraction grating and slits to select five wavelengths in the UV spectral band. The instrument mechanically tracks the sun during the day, measures UV intensity at all selected wavelengths and calculates total ozone and total SO₂. The spectrophotometer is controlled by an external PC and provides practically continuous data without an observer present. This instrument generally requires more advanced and frequent technical

maintenance support than the Dobson due to its high technology components and fully automated operation.

The M-124 ozonometer uses narrow band filters to select wavelengths appropriate to apply the same differential absorption principle as the Dobson spectrophotometer. These instruments are less expensive, but also less accurate than the Dobson and Brewer spectrophotometers. They have been used successfully in the countries of the former Soviet Union for more than 25 years.

Similar UV filter instruments like M-124 have been developed and commercially offered in recent years. Although some of them come from recognized producers they are not recommended for long-term monitoring of total ozone.

Generally a minimum of 3 measurements of total ozone are needed to obtain a station daily average. International protocol requires that each station produce a daily report of each days measurements, with coded information indicating wavelength and observation conditions. The daily averages or individual observations are reported to WOUDC usually each month, mainly by electronic transmission.

QA/QC

The World Dobson Calibration Centre located at NOAA CMDL Boulder, Colorado, USA has assumed the lead role in the operational aspects of Dobson intercomparisons. They maintain the World Reference Standard Dobson (No. 83) in Boulder and frequently check the calibration of the secondary standard Dobson spectrophotometer (No. 65), that is generally used for intercomparisons. The Regional Dobson Calibration Centre for Europe (Region VI) performed its first intercomparison campaign during 2000 in its new dedicated Dobson facility at the Meteorological Observatory in Hohenpeissenberg, Germany. Centres for Asia (Region II) and the South-West Pacific (Region V) have also been established in Tsukuba, Japan and Melbourne, Australia. Regional Dobson Calibration Centres are anticipated for Villa Ortuzar, Buenos Aires, Argentina (Region III) and Pretoria, South Africa (Region I) following the successful intercomparisons that were held in those locations in late 1999 and early 2000.

Ancillary Measurements

No ancillary measurements are required although observations of the sky cloud cover are needed.

Archiving Procedures

Upon receipt, station data are recorded in the GAW central archive (WOUDC) and available soon afterward to the general scientific community. Preliminary data are indicated as such at the time of submission, and are frequently submitted for near-real-time applications such as the mapping of the Antarctic ozone hole. If required by data originators the data deposited in WOUDC can be maintained there under access restrictions defined in agreement with the Manager of the WOUDC database. Data can be accessed through the WOUDC web site.

Data Analysis

Processing of total ozone observations, QA/QC procedures, data management and submission of results to WOUDC represent a system of operations now carried out mainly with PCs at stations. To cover these needs a data analysis software package has been created and made available for general use by the Solar and Ozone Observatory (SOO-HK) of the Czech Hydrometeorological Institute in Hradec Kralove.

Application of the Results

Ground based total ozone data have played a critical role in documenting the major changes in the ozone layer going back several decades, particularly in identifying the Antarctic ozone hole and its temporal and spatial evolution. These measurements continue to play a central role in documenting ozone changes on global and regional scales. They have also been used as an independent check on the global satellite measurements of total ozone and they also help in ozone data assimilation for large-scale circulation forecasting models.

Equipment and Infrastructure Cost (US \$)

Dobson spectrophotometer -approx. 100,000
(New instruments are not currently available commercially)

Calibrations are required every 3-4 years, and are made available at regional Dobson calibration centres through the WMO and participating Member countries throughout the world.

Brewer spectrophotometer -approx. 100,000
Calibrations are required every 1-2 years and are available commercially.

M-124 Filter ozonometer – approximately \$15,000 USD
(New instruments are not currently available commercially)
Calibrations are provided by the Main Geophysical Observatory of the Russian Federal Service for Hydrometeorology and Environmental Monitoring in St. Petersburg and are required every 2 years to maintain the accuracy required.

Personnel Requirements and Training

Personnel: Operator - 1 hour per day
Training: Dobson/Brewer for global observations -2 weeks
Dobson training is available on a space limited basis at SOO-HK
Brewer maintenance requires high technical abilities.

References

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2.2.2. Ozonesondes

Importance

Ozonesondes are the primary source of information available for ozone vertical distributions in the free troposphere and lower stratosphere. Ozone variability in these regions is very high thus requiring frequent measurements to represent these variations adequately in models and evaluate long term changes that are occurring.

Siting Requirements

Ozonesondes are small, lightweight and compact balloon borne instruments, coupled via interfacing electronics with radiosondes for data transmission and additional measurements of meteorological parameters like pressure, temperature with optional measurements of humidity and winds. Total weight of the flight package is less than 1 kg which can be flown on small latex weather balloons. The data measured by the sonde is telemetered to the ground station for further data processing. Ozonesondes can be launched from almost any place in the world where the necessary support equipment is available. Balloons require a source of helium (tanks brought to the site) or hydrogen (provided by a generator at the site). The intercomparison of the sonde integrated column with ground based total column measurements provides a good indication of the quality of the measurements. Often, the measured total ozone column is used to adjust the sonde profile. For this reason, a nearby Dobson or Brewer total column ozone station is highly desirable.

There is a shortage of long-term ozonesonde stations around the world, but the shortage is particularly acute in the tropics and much of the Southern Hemisphere. Due to the high expense of launching once a week ozonesondes, the selection of suitable sites should also be based upon studies of the expected scientific contribution from each potential site. However, ozonesondes can be easily supported by existing radio weather sounding systems.

Methods of Measurement and Sampling Frequency

Ozonesondes commonly in use utilise electrochemical detection methods. The most widely used are the so called ECC (electrochemical concentration cell) sondes. Although more commonly used in the past, the somewhat similar Brewer-Mast sondes are presently used by only two long term stations. Two other electrochemical sonde types have been developed, one by the Japan Meteorological Agency and the other by the India Meteorological Department. These ozonesondes are commonly used in these two countries. Differences between sonde types are significant when considering operating procedures, costs, and reliability of the data, although all use electrochemical methods.

QA/QC

At this time, stations use a variety of techniques to prepare the sondes and analyse the data, thus producing station to station differences in ozone that do not reflect actual variations in ozone. Referencing of sondes to total column measurements is also not standardised. Since 1996, there has been a series of chamber campaigns (Juelich Ozone Sonde Intercomparison Experiment or JOSIE), with the last one in September 2000, with the objective of obtaining a better understanding of the operational differences between all types of sondes. Standard operating procedures (SOPs) are presently under development using the environmental chamber and reference ozone photometer at the World Calibration Centre for Ozone Sondes in Juelich, Germany.

Ancillary Measurements

Total column ozone and surface ozone measurements are highly recommended at or near all ozonesonde sites.

Archiving Procedures

Final data are submitted, usually monthly, to the World Ozone and Ultraviolet Radiation Data Centre (WOUDC) in Toronto, Canada. In some situations preliminary near-real-time data are submitted either to regional data centres or WOUDC.

Data Analysis

Ozonesonde data are generally reduced real-time into preliminary data as the data are acquired by the sonde ground station receiver or shortly after. Later, when total column data are available, final data are verified and archived.

Application of Results

Tropospheric climatology (long term changes); biomass burning; long-range transport. Stratospheric polar loss, variability vertically and seasonally and transport including stratospheric tropospheric exchange

Equipment and Infrastructure Cost (US \$)

One balloon flight package (includes ozone and radiosondes plus interfacing electronics, balloon and gas). Total cost 600-800.
Ground station equipment costs about 30,000

Personnel Requirements and Training

To prepare and conduct an ozone sounding, one technician with some experience in meteorological instrumentation and training in simple chemical laboratory handling is required. To perform an ozone sounding, pre and post flight operation takes about 8 hours. Training for performing an ozone sounding will take from 2 to 4 weeks at a sounding site.

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2.2.3. Surface Ozone

Importance

Ozone measured at the earth's surface plays a key role in the chemical cycling of gases in the troposphere, and it contributes to greenhouse warming. Its concentrations appear to be increasing due to human activities and careful measurements must be made to verify these changes and track those that may occur in the future. Although ozone is not a primary pollutant (i.e. not emitted directly by human activity), it is produced through the action of sunlight on primary pollutants such as nitrogen oxides and hydrocarbons. The influence of anthropogenically produced ozone on the global ozone budget is a primary focus of current research.

Siting Requirements

Because ozone is a reactive gas, measurements in many locations are required to define its spatial and temporal variations. Near sources of industrial pollution or biomass burning, ozone concentrations are generally elevated due to photochemical production. At sites more remote from these primarily anthropogenic influences, background measurements may be representative of broad geographic regions.

The elevation of a site may be an important factor in determining the type of measurement obtained. For example, stations located at high elevation mountain sites are frequently representative of the free troposphere. At boundary layer sites in marine environments, photochemical losses usually dominate while stations downwind of pollution sources will measure higher values of ozone. Because of this high variability of tropospheric ozone, many stations are required to adequately determine and assess its global distribution.

Methods of Measurement and Sampling Frequency

Several methods of ozone measurement have been used to gather in-situ ozone records. Ultraviolet photometry is regarded as the preferred method because of its high accuracy, stability, freedom from interference, and ease of operation. UV-photometry-based ozone monitors are available from commercial manufacturers. The basic measurement principle is the attenuation of UV light at a wavelength of 254 nm due to the presence of ozone in a flowing air sample. The instruments measure the relative attenuation between an air sample in which only the ozone is removed and one in which ozone is present. With a knowledge of the sample path length and the UV absorption coefficient of ozone, the ozone concentration is determined. Measurements using a UV ozone monitor are virtually continuous.

In principle, this method is highly accurate, but instrument defects or degradation of components, such as the catalyst used to destroy ozone in the reference portion of the measurement cycle, will adversely affect the accuracy. Commercially available ozone generators are less stable than ozone monitors, and do not provide adequate standards for checking instrument accuracy.

QA/QC

The data quality objectives for surface ozone measurements are defined in GAW Report No. 97 [1.2]. The quality of the measurements relies on proper maintenance and intercomparison of the instrumentation (i.e., traceability to the designated international reference) as well as proper documentation of all activities.

On a daily to weekly schedule, the instrument is given a "zero" check by sampling air with ozone removed to determine the zero level of the instrument. A "span" concentration can also be provided to the instrument to check its operation. Such span samples should not be used to calibrate the instrument but may indicate instrument malfunction. All maintenance procedures and intervals are recommended by the manufacturer of the instrument and outlined in GAW Report No. 97.

All data should be routinely inspected by the trained operator in order to flag erroneous measurements.

Internal intercomparisons by the station operator with a NIST-traceable ozone calibrator are recommended every 6 months to determine possible instrument malfunction. Periodic intercomparisons between an instrument maintained as a network standard and the station instrument provides one means of ensuring an instrument's accuracy and making corrections to station instrument records. The network standards are linked to a recognised international standard reference ozone photometer maintained at the National Institute of Standards and Technology in Gaithersburg, Maryland, USA. Full traceability of measurements by the designated field instrument to the international reference will be ensured by the designated Calibration Centre on a biannual basis, if feasible.

Ancillary Measurements

Recommended ancillary measurements include standard meteorological measurements and a tracer for local pollution such as continuous measurements of CO, NO or aerosol absorption by e.g., aethalometer.

Archiving Procedures

In addition to the ozone data, meteorological and other meta data should be recorded as recommended by the WDCSO.

Data Analysis

Most of the ozone monitors are capable of producing both digital and analogue outputs which readily allow recording on PC based data systems or chart recorders. Data usually require some screening to ensure proper background measurements are being made, and to ensure that the instrument is functioning properly. The ozone measurement is usually expressed as mixing ratio, which requires a measure of the temperature and pressure within the sample chamber. Ozone monitors usually include these measurements and do the mixing ratio calculation automatically. The data are normally submitted as 30 minutes averages and deposited into the WDCSO at NILU, usually once a month.

Application of Results

Although surface ozone data are often community used to assess air quality and related public health issues in urban environments, the primary purpose of surface-based ozone measurements in the GAW network is to develop an understanding of lower tropospheric ozone and its global distribution in rural environments. For example, the data can be used to test model calculations of the chemistry and transport of ozone in the remote atmosphere. Data at regional stations are used to help evaluate the impact of ozone concentrations on the regional environment.

Records over periods of decades have been analysed to investigate possible anthropogenic influences on the oxidative state of the atmosphere and the possible effects of tropospheric ozone increases on greenhouse warming of the atmosphere.

Equipment and Infrastructure Cost (US \$)

UV Ozone Monitor

Monitor with data system about 15,000

network standard about 15,000

Various annual costs including inlet filters and instrument repairs when required - about 300 per year.

Personnel Requirements and Training

Personnel: Station operator one half day per week

Training: Operator for station instrument one week

References

WMO GAW Report No. 97, Quality Assurance Project Plan for Continuous Ground Based Ozone Measurements.

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2.3 Reactive Gases

2.3.1 Carbon Monoxide

Importance

In the non-urban troposphere, carbon monoxide (CO) is often the primary sink for hydroxyl (OH) radical. It is therefore an intimate component of the series of photochemical reactions which ultimately oxidize reduced carbon-, nitrogen-, and sulfur-containing trace gases. Although CO itself does not contribute directly to the greenhouse effect, because of its influence on OH, CO has climatological importance as its abundance indirectly affect the abundances of other greenhouse gases such as methane.

Site Requirements

The atmospheric lifetime of CO varies from weeks to months depending on OH concentrations. As a result, there are relatively large differences in CO mixing ratios determined on regional scales. CO levels in the marine boundary layer range from a high of approximately 250 ppb (parts per billion) in the Northern Hemisphere winter to a low of 40 ppb to 50 ppb during the Austral summer. There can also be a considerable variation in the mixing ratio between continental and oceanic areas. Estimates of the long-term rate of change of CO vary widely: from 6% per year (best estimate, 1-2%) in the Northern Hemisphere to no significant change in the Southern Hemisphere. Recent observations indicate that atmospheric CO abundance is quite variable from year to year, reflecting the variable nature of its emissions. Measurements at established background sites will define geographical distributions and establish growth rates, but additional measurements at sites located closer to major sources (industry, transportation, and biomass burning), and measurements above the planetary boundary layer, are necessary to define postulated global budgets of this gas.

Methods of Measurement and Sampling Frequency

Several analytical techniques are available with which to measure CO at atmospheric levels. Measurements can be made by gas chromatography, with either a flame ionization detector or a mercuric oxide reduction detector. Two columns are typically used in series; first a silica gel column for the removal of impurities, followed by the separation of CO, H₂ and CH₄ on molecular sieve 5A. Using FID, CO is catalytically converted to CH₄ before entering the detector. In this case, the same GC can be used to measure both CH₄ and CO (and other hydrocarbons as well). A measurement precision of 5-10% is easily obtained. In the HgO reduction detector, CO reacts with hot HgO releasing Hg vapor, which is detected by resonant-UV absorption. Molecular hydrogen is also detected with this method. Precision is on the order 1-2%. HgO detectors are often non-linear in their response over the range of atmospheric CO levels, however this problem is minimized through the use of multiple calibration standards. GC methods require calibration of the instrument to quantify CO mole fractions in samples.

Another method commonly used at remote sites to measure atmospheric CO is Gas Filter Correlation Radiometry (GFC). GFC is a Non-Dispersive Infra-Red (NDIR) technique that measures CO continuously, rather than every few minutes as by GC. GFC can achieve precisions of 5-7% when averaging over 1 hr. Calibration of the instrument is also required.

Tunable diode laser spectroscopy (TDLS) also measures ambient levels of CO by infrared absorption. Drawbacks of this method are that the start-up costs are much greater than for GC or GFC, a high degree of technical skill is required to maintain the instruments, and TDLS is not well suited for remote operation. The absorption of solar radiation by CO is the basis of another measurement technique. This technique is used to obtain the total-column abundance of CO.

Standards consisting of dried air with carefully determined CO mole fractions are essential to programmes that use GC, GFC, or TDLS to measure CO. In the past, it has been difficult to

obtain CO standards representing atmospheric levels. Recently, the WMO designated CMDL (Climate Monitoring and Diagnostics Laboratory) NOAA in Boulder, Colorado, as the central calibration facility for CO. CMDL will work in coordination with the Fraunhofer Institute (Garmisch-Partenkirchen, Germany) and the Nitrous Oxide and Halocarbons Group of NOAA/CMDL to provide the research community with high-quality CO standards. However, caution must still be used when comparing previously obtained data sets from various laboratories to evaluate either geographical or temporal CO changes. This is primarily due to the use of different standard scales which may vary by as much as 30%. There can be a very significant instability of CO during storage of discrete flask samples. (Flask samples of air are generally analyzed using one of the GC methods). CO may increase or decrease significantly in a few days to weeks in many types of containers. Methods and materials should be rigorously tested before beginning field measurements.

QA/QC

Many activities are required to insure high-quality CO data. At the highest level, these activities include maintaining an internally-consistent standard gas scale and frequent scientific scrutiny of the data. Regular scientific scrutiny of the data can only occur if a reasonable data base management system and graphics capability to view data in near-real-time are in place. Experts should regularly examine plots of the data to insure the values are reasonable, and to begin searching for the reasons if they are not.

Quality control can also be enhanced by scrutinizing “engineering data” recorded from an analysis system such as pressures, temperatures, and flow rates. With chromatographic methods, additional QC information is available from chromatographic parameters that include peak retention time and peak width.

It is essential for measurement programmes to have redundancy built into them. When inconsistencies appear among duplicate measurements, then the search for the cause can start. Some examples of precautionary measures are:

1. Carefully collect discrete samples that can be compared with in situ measurements. Normally analyse at a central laboratory that also maintains a programme’s highest level standards.
2. Routinely analyse air from a “surveillance” cylinder as part of an in situ measurement programme, (e.g., randomly once per day).
3. For in situ operations, use two different intake lines. If one intake has a leak inside the observatory building, it will be obvious.
4. Analyse “test” samples from flasks that were filled from a cylinder of natural air. These test flasks should be analysed every day that discrete samples are analysed.
5. Share samples with other measurement programmes and routinely compare results.

There is no universal scheme to insure high-quality data; each programme should develop a scheme, with guidance from other successful programmes, suitable to their own needs.

Ancillary measurements

The most important ancillary measurements are meteorological data including, wind speed and direction, temperature, dewpoint, and pressure.

Archiving Procedures

CO data are archived at the Carbon Dioxide Information and Analysis Centre in Oak Ridge, USA, and since 1990, with the WMO World Data Centre for Greenhouse Gases, operated by the Japan Meteorological Agency in Tokyo.

Data Treatment

For GC methods, instrument response is integrated and peak responses for samples and standards are recorded digitally. Using GC, GFC or TDLS, all CO mole fractions are determined using the instrument response of the sample relative to that of the standard(s). Detectors with non-linear response must use multiple standards to account for the non-linearity. The CO data are examined for instrument malfunctions, and note of these made in the data files. Then several criteria (e.g., wind direction, wind speed) may be used to select data considered to be unrepresentative of "background" air (that is air not representing mixing ratios over a large area). No data are removed from the record, they are only classified by alphanumeric "flags".

Archiving Procedures

Both flask data and data from field instruments are archived with the WMO World Data Centre for Greenhouse Gases (WDCGG), operated by the Japan Meteorological Agency located in Tokyo, Japan. CO data may also be archived at the Carbon Dioxide Information Analysis Centre (CDIAC) in Oak Ridge, TN, USA.

Application of Results

The CO data can be used to increase our understanding of changes in the oxidation processes that are occurring in the atmosphere. The observations will also provide limits on hypothesized global budgets of CO.

Equipment and Infrastructure Cost (US \$)

Field Instrument - Remote Global Station

GC or GFC	10-17,000
Data Acquisition	5,000
Gas Handling	3,000
Reference gases	5,000
Total startup costs	23 - 40,000

Maintenance:

Standard Gases	5,000 per year
Supplies and maintenance	6,000 per year

Flask Sampling at Remote Sites

(costs dependent on number of sites)

Flasks (20) and sampler (1)	-	6,000 per site
Logistics	-	3-5,000 per year, per site
Central Laboratory	-	40,000 (start-up, 1 year)
	-	11,000 (supplies and maintenance)

Personnel Requirements and Training

Personnel: Central laboratory, one full-time person, depending on number of sites and sampling frequency
Field instrument, 1 man-month per year
Collection of flask samples, 1-2 hours/week

Training: GC operator, 3 months
Sample taker, 2 days

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2.3.2. Sulphur Dioxide

Importance

Sulphur dioxide (SO₂) is a greenhouse gas because it is an infrared absorber. But, because of its low concentration relative to other greenhouse gases it is less significant. It is a climatically active trace species, because atmospheric SO₂ reacts photochemically (homogeneous conversion) and on airborne particles (heterogeneous conversion) to produce sulphates. Atmospheric sulphate particles are active cloud condensation nuclei. An increase in the number of cloud condensation nuclei on a global scale may increase cloud albedo. An enhancement in atmospheric sulphate particles in the stratosphere may increase short-wave reflection to space.

Sulphur dioxide also plays a significant role in producing acid deposition by forming sulphate particles. These particles return to the Earth's surface via dry or wet deposition processes. Both processes transfer excess acidity to their deposition sites. This acidity may damage sensitive ecosystems.

SO₂ has not been routinely monitored at GAW Global stations so far, but is a standard measurement at a number of regional stations. The concentration of sulphur dioxide in remote areas is about .05 ppbv. In urban areas, concentrations may rise to greater than 10 ppbv. Power plant plumes and volcanic emissions may emit concentrations as high as 1 000 ppbv.

Siting Requirements

The sources for SO₂ in the atmosphere include the sea, volcanic activity, anthropogenic emissions, and biomass decay processes. Measurements to monitor the background concentration of SO₂ should be made far away from sources. Careful placement of the SO₂ monitoring lines should be considered in order to reduce contamination from local sources, such as traffic, and heat/power generators. SO₂ is a reactive gas with an atmospheric lifetime of hours to days. It may stick to intake lines or oxidize within water drops condensed in the lines. Thus, intake lines should be made of inert material (Teflon, stainless steel) and be as short as possible.

Measurement Methods and Sampling Frequency

SO₂ concentrations can be measured continuously using either a pulsed-fluorescence analyser or a flame-photometric device. Even though the response of the pulsed-fluorescence sensor is slower, its ease of calibration, dependability, accuracy, and SO₂ specificity make it preferable. More sensitive gas chromatographic techniques are also available. However, they require significant technical expertise and regular attention. SO₂ concentrations can also be measured using filter media. This method yields a potentially more accurate result, but it is an integrative technique with lower resolution time, typically one day, requires frequent attention, and filter analysis man power costs are high.

Since SO₂ has a short atmospheric lifetime, understanding the sulphur cycle requires knowledge of the source and sink terms. This is best accomplished with sampling frequencies of less than 1 hour. Therefore, the best technique for long-term monitoring of SO₂ may be a combination of the pulsed-fluorescence analyser and filter sampling. Filter samples would be exposed at intervals, but often enough to act as a quality control for the continuous analyser.

QA/QC

The quality of the measurements relies on proper maintenance and calibration of the instrumentation as well as proper documentation of all activities. Zero checks and calibrations should be performed at regular intervals. Raw data should be (quality-)inspected by a trained operator to facilitate flagging of erroneous measurements and data validation. All maintenance procedures and intervals as recommended by the manufacturer of the instrumentation should be carefully observed.

Collecting impregnated filter samples is an alternate method. This can also be used for QA of the continuous monitoring methods. [See for example: EMEP manual for sampling and chemical analysis]

Ancillary Measurements

Recommended ancillary measurements include an array of meteorological measurements.

Archiving Procedures

Sulphur dioxide has not been monitored regularly at GAW Global stations, except as a part of acid deposition studies. The SO₂ measurements for GAW stations are archived at the WMO World Data Centre for Greenhouse Gases, operated by the Japan Meteorological Agency in Tokyo. The data appear as average SO₂ concentration (ppbv) in selected time intervals. The reporting of an average concentration at 10-minute intervals (continuous analyser) or 1-day intervals (filter system) is appropriate and feasible.

Data Analysis

Continuous SO₂ samplers usually produce an analog voltage output. The voltage is proportional to SO₂ concentration, frequently with a zero-offset. The zero value of the continuous monitor drifts with time, in response to changing pressure, temperature, and humidity conditions. The voltage to concentration algorithm is found via periodically calibrating the monitor with known concentrations of SO₂. Data reduction consists of applying appropriate zero values and appropriate voltage to concentration conversion equations as functions of time.

Filter pack sampling systems consist of filters exposed to a known volume of ambient air. Exposed filters are digested and sulphate is determined from the aliquot by a suitable method. Ion chromatography is recommended. The difference in sulphate of exposed and blank filters is the exposure total. The exposure total divided by the volume of ambient air drawn through the filter yields the average SO₂ concentration in the air.

Application of Results

Average SO₂ concentrations may be coupled with emission inventories, sulphate conversion rates, and deposition rates to refine our knowledge of the atmospheric sulphur cycle. These refined assessments may be used to predict regions where atmospheric sulphur concentrations and hence acid deposition or cloud albedo are likely to change. This knowledge can help guide policymaking with regard to emission control.

Equipment and Infrastructure Cost (US \$)

SO₂ In-Situ Sampler

Analyser - 15,000 (capital cost)
Calibrator system - 8,000 (capital cost)
Calibration gases - each 1,000
Total start-up cost - 24,000
Variable annual costs to maintain system, calibration gases, etc.

SO₂ Filter-Pack Sampler

Filter sampler - 10,000 (one-time cost)
Total start-up cost - 10,000
Filter analysis – 10-20 per sample
Variable annual costs to maintain system

Personnel Requirements and Training

Personnel: Chemist to install and calibrate system at site - 2 weeks
Technician to check system, change calibration gases, and change filter media - 3 man-months per year
Analyst to apply calibration corrections, provide quality control, and archive collected data - 2 man-months per year

Training: Technician - 2 weeks

References

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2.3.3. Nitrogen Oxides

Importance

Nitrogen oxides form a large family of trace gases that are ubiquitous in the Earth's troposphere. They originate from both anthropogenic (combustion) and natural (biomass burning, lightning, soil microbial activity) processes; transport from the stratosphere is also thought to be a source. Nitrogen oxides play a crucial role in determining the ozone concentration in the air; they can also contribute to acid precipitation. Although the need for knowledge of the abundance of these compounds is unquestioned even at the pptv level (1 pptv = 1 in 10^{12} molecules), very little observational data outside urban areas are presently available. The more important compounds are NO, NO₂ (the sum of these two compounds is usually indicated as NO_x), HNO₃, aerosol nitrate, and peroxy-acetyl-nitrate (PAN). NO and NO₂ are the initial compounds emitted, while the others are secondary products resulting from atmospheric conversions.

Nitrous oxide (N₂O) is a special case; its chemistry is very different from all other nitrogen oxides in that it is essentially inert in the troposphere. It is discussed separately as part of the greenhouse gases (Section 2.1.4).

Nitrogen oxides have not been routinely measured at global sites. Conversions between the different compounds are generally rapid, and the only unambiguous data for nitrogen oxides would be the sum of all compounds (excluding N₂O), which is often denoted as "NO_y". Since anthropogenic activities constitute a large source of nitrogen oxides, any true background signal can be observed only at very remote locations.

Siting Requirements

Siting requirements are dependent on the type of information that is sought. Obvious precautions related to human interference with the measurements have to be taken. Since the levels are so low even at less remote locations, great care has to be taken to minimize potential contamination from any form of motorized transportation, which is a principal source of NO_x.

Methods of Measurements

NO, NO₂: Reliable measurements of these compounds at background levels have only been possible with instruments that are based on chemiluminescence of NO (with ozone) or NO₂ (with luminol solution). The other compound (NO₂ or NO, respectively) is then measured by converting it into the principal luminescing compound. Unfortunately, the first method (NO chemiluminescence) requires carefully designed special equipment, while the other method so far has not been very successful for long term measurements at all, largely due to technical and interference problems. A further major problem is to ascertain that the conversion of NO₂ into NO, or vice versa, is unique.

PAN: A few long-time records on PAN have been collected, based on automated gas chromatography, equipped with electron capture detection. The major problem with this method is the unreliability of calibration. Standards have to be made in the laboratory and have to be carefully calibrated, which is usually done by infrared spectroscopy or ion chromatography. These standards have a relatively short lifetime, and frequent calibration is therefore impractical for long-term monitoring. An alternative calibration method involves the generation of PAN by photolysis of excess acetone and NO in zero air. NO is used as the concentration-determining compound. This allows PAN measurements to be directly linked to NO standard gases. This technique is commercially available, and has proven to be more reliable and practical for long-term monitoring.

HNO₃, aerosol nitrate: These compounds are amenable to monitoring with filters. A standard procedure involves a train of filters in series, with the first filter being a Teflon filter to capture aerosols, including aerosol nitrate, followed by a nylon or base-impregnated filter to capture acidic gases including HNO₃. These filters are routinely exposed for periods of at least 24

hours by sucking through air at a flow rate of several litres per minute. The filters are then transported to a laboratory, extracted, and analysed for nitrate ions by ion chromatography. To derive the amount of air that is sampled, the pumping flow rate has to be continually measured.

NO_y: The sum of all nitrogen oxides is measured after full conversion to either NO or NO₂ and by measurement of the latter compounds as described earlier. This conversion is obtained by sucking air through a gold-coated converter tube kept at ca. 300 °C, together with a small amount of either pure carbon monoxide or hydrogen gas. Alternatively, a molybdenum tube at similar temperatures can be used, although its efficiency of conversion is somewhat controversial.

QA/QC

All of the above described measurement techniques require special QA/QC procedures. In general, the quality of the measurements relies on proper maintenance and calibration of the instrumentation (i.e., traceability to the designated international reference) as well as proper documentation of all activities. Raw data should be (quality-)inspected by a trained operator to facilitate flagging of erroneous measurements and data validation. All maintenance procedures and intervals as recommended by the manufacturer of the instrumentation should be carefully observed.

NO, NO₂, NO_y: On a daily to weekly schedule, the instrument is given a “zero” check by sampling air with nitrogen oxides removed to determine the zero level of the instrument. A span concentration should also be provided to the instrument for calibration purposes. Additionally, the converter efficiency should be checked regularly. For NO_y the inlet system should be as short as possible. Regular checks of HNO₃ loss in the inlet should be performed.

PAN: With the chromatographic method, additional QC information is available from chromatographic parameters that include peak retention time and peak width.

HNO₃, aerosol nitrate: Comparisons with other techniques, e.g., denuder methods, may help to improve the data quality. The measurement system should be regularly checked for artifacts, e.g., loss of aerosol nitrate on teflon filters.

It must be stressed that there is no universal scheme to insure high quality data. Each programme should develop an individual scheme, with guidance from other successful programmes, suitable to their own needs.

Ancillary Measurements

Recommended ancillary measurements include an array of meteorological Measurements. Surface ozone and CO are also useful for the interpretation of the measurements.

Archiving Procedures

It is common procedure to archive all raw field data, in addition to a final data set that is reduced to a longer averaging period. The averaging period depends on the anticipated use of the data and varies from 5-10 minutes to daily or monthly averages. The nitrogen oxides measured at GAW stations are archived at the WMO World Data Centre for Greenhouse Gases, operated by the Japan Meteorological Agency in Tokyo.

Data Analysis

All instrumental methods require an electronic data system; the use of a chart recorder as a backup is highly recommended. Flow rates for filter sampling procedures need similar data storage. In the laboratory these records have to be carefully screened for any periods of time for which the data are invalid due to human interference (usually any visit of an operator to the monitoring site influences the

data); periods that calibrations were performed have to be removed from the record as well. Normally, the raw field data are corrected for calibration data in the laboratory, to yield a final data set.

Application of Results

In view of the importance of these data for understanding global tropospheric ozone patterns, the scientific community needs good quality nitrogen oxides data, which is not available to the extent required.

Equipment and Infrastructure Cost (US \$)

NO, NO₂:

Analyser (NO₂ photolytic converter, O₃ chemiluminescence) - 60,000
(NO CrO₃ converter, luminol chemiluminescence) - 20,000
Calibration system (NO₂ permeation) - 15,000
NO calibration gas, each - 1,000
Data system (data logger, computer, chart recorder) - 12,000

PAN:

Gas chromatograph with electron capture detector - 20,000
Data system (integrator, logger, computer, chart recorder) - 10,000
Calibration system linked to NO standards - 20,000
NO calibration gas, each - 1,000
Calibration system - 10,000
Central Laboratory arrangement to prepare standards. Needs access to FTIR, HPLC, or ion chromatography equipment for absolute standardization

HNO₃, aerosol nitrate:

Filter sampling system (filter packs, pump, flowmeters, loggers) - 20,000
Needs Central Laboratory to prepare and analyse filters.
Costs exclusive initial laboratory setup, per annum - 50,000

NO_y:

Analyser ("NO_x-box") - 30,000
Converter for NO_y measurements - 30,000
Data system (data logger, computer, chart recorder) - 12,000
Calibration system (NO₂, HNO₃ permeation) - 15,000

NO calibration gas, each - 1,000

All systems have various annual maintenance costs including special supplies, etc.

Personnel Requirements and Training

None of these measurements can be done on a routine basis, with the possible exception of the filter sampling for HNO₃ and aerosol nitrate. Site operators can be trained in a short time span, but realistically they can only be expected to perform the filter-pack sampling.

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3. AEROSOLS AND OPTICAL DEPTH

Introduction

It is the goal of GAW to ensure long-term measurements in order to detect trends and reasons for them (WMO, 1997). 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 up to multi-decadal time scales. While much of the recent international focus has been directed at assessing the impact of human activities on regional and global scales, there is growing recognition that the management of urban environments requires special attention, and has resulted in an increasing interest in regional air quality within WMO.

Airborne aerosols affect many aspects of human health and the environment. Aerosol mass and its toxicity are known to have links to chronic respiratory and acute cardio-vascular problems. Aerosols are also tightly linked to problems of visibility reduction, acid rain, and urban smog in many locations of the world. Furthermore, aerosols influence the atmospheric energy budget through direct and indirect effects. Direct effects refer to the scattering and absorption of radiation and their subsequent influence on planetary albedo and the climate system. Indirect effects refer to the increase in available cloud condensation nuclei (CCN) due to an increase in anthropogenic aerosol concentration. This is believed to change the cloud droplet number concentration for a constant cloud liquid water content (LWC), and the resulting increase in cloud albedo influences the Earth's radiation budget. Cloud lifetimes and precipitation frequencies are also thought to be affected. Despite the uncertainty, it is believed that in regions with high anthropogenic aerosol concentrations, aerosol forcing may be of the same magnitude, but opposite in sign to the combined effect of all greenhouse gases. More information may be found in IPCC (1995).

The scale of these impacts depends on the aerosol particle sizes. On a mass basis, the tropospheric aerosol is generally dominated by two populations of particles, with characteristically different sources, sinks, sizes and chemical compositions. The submicrometer fraction ("fine particles") generally originates from condensation sources (both high and low temperature) and from atmospheric gas-to-particle conversion processes, and is primarily removed by precipitation. In contrast, the supermicrometer fraction ("coarse particles") is produced by mechanical processes (soil erosion, seawater bubble-bursting), and is mainly removed by sedimentation and has a considerably shorter atmospheric residence time than the submicrometer fraction. Size-segregation therefore allows the determination of the aerosol properties of each of these two populations so that their atmospheric effects can be evaluated separately. It also provides data that can be used to validate models used as the scientific basis for policies dealing with related issues.

Since the atmospheric residence time of aerosol particles is relatively short, a large number of measuring stations are needed. GAW consists of 22 Global stations which cover different types of aerosols: Clean and polluted continental, marine, arctic, dust, biomass burning, and free troposphere. Recently, the Scientific Advisory Group (SAG) for Aerosols and Optical Depth within GAW made additional recommendations, mainly concerning better coverage of the polluted continental aerosol type. While Global stations are expected to measure as many of the key variables as possible, the approximately 300 GAW Regional stations generally carry out a smaller set of observations.

According to the recommendations of the SAG, Regional stations should measure the optical depth, mass concentration and major chemical components in two size fractions, and the light scattering coefficient. Those stations wanting to add aerosol number concentrations for health effects are advised to do so.

At Global stations, a larger number of measurements are envisaged. These include the Regional parameters list and in addition, the light scattering and hemispheric backscattering coefficients at various wavelengths, the light absorption coefficient, aerosol number concentration,

cloud condensation nuclei (CCN) concentration at 0.5% supersaturation, and diffuse, global and direct solar radiation. Additional parameters such as the aerosol size distribution, detailed size fractionated chemical composition, dependence of aerosol properties on relative humidity, CCN concentration at various supersaturations, and the vertical distribution of aerosol properties should be measured intermittently at Global stations.

Short summaries of selected parameters are presented below. The measurement of some parameters is not described further here due to space restrictions, and because it is felt that those parameters should best be accompanied by a scientific programme. The interested reader is referred to the full GAW Guide for Aerosols. It should be noted at this point that suitable instrumentation is not presently available for some parameters, and some calibration procedures require further international research efforts and coordination. An important part of these activities is planned for the World Aerosol Calibration Centre, however, there are still funding problems with this facility.

At the core of the GAW network of Global and Regional stations is a willingness on the part of the participating organizations to pool their observations and make them publicly available. Public access to the aerosol observations made within GAW is provided by the World Data Centre for Aerosols (WDCA) hosted by the Environment Institute of the Joint Research Centre, Ispra, Italy (EU). The detailed arrangements for submission of data are contained in the GAW Guide for Aerosols, so the following is a statement of the principles of data archiving that reflects the Aerosol Guide.

GAW participants endeavor to provide precise, accurate and timely observations of the aerosol parameters detailed below. In order to achieve this and as important information for the user community, the data available from the WDCA should have certain properties:

1. They should be traceable to the original observation signals. This obligates 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 a 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. Key data descriptors are identified in the following descriptions of the parameters, and will be detailed in full in the GAW Aerosol Guide.
4. 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.

General Sampling Considerations

Inlet Design Considerations

In this section we provide a procedure for common sampling considerations that apply to most of the aerosol analyzers and samplers at Global and Regional GAW stations. The inlet used for aerosol sampling at GAW sites must follow certain design guidelines so that comparable samples are obtained. 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. Specifically, it is desired to maintain comparability in relative humidity because of the need to provide a uniform specification of the aerosol sampled by various analyzers and samplers at a given location and at different atmospheric field stations, in view of the strong influence of the relative humidity on the size of hygroscopic particles. It is necessary to control height above terrain and vegetation to obtain representative samples free of near-surface dust contamination. Likewise, it is necessary to exclude precipitation because of its interference with the measurements.

Aerosol sampling equipment should be housed in a shelter that provides a controlled environment (temperature 15-30°C). Sample air should be brought into the instrument housing through a vertical stack with an inlet that is well above ground level. For sites in level terrain, surrounded by no or low vegetation, a height of 5-10 m above ground level is recommended. However, some sites may require higher inlets to avoid an influence by the surroundings. If possible the sampling duct should be brought through the roof of the instrument housing. If this is not possible, then a slight bend in the inlet pipe is acceptable. Because gas analyzers may have incompatible requirements, a dedicated inlet stack may be required for the aerosol samples.

An omni-directional aerosol inlet is required. This can be achieved with a vertical configuration. The size of the entrance configuration must be well designed to provide a high inlet sampling efficiency for aerosol particles over a wide range of wind speeds. The cut-off diameter of the inlet and sampling line should match the US-PM10 standard (ambient conditions) as close as possible. At 10 m/s wind velocity, a 10- μm particle has a stopping distance of 0.23 cm. The inlet design must thus consider dimensions five times larger than the stopping distance to avoid particle losses.

A cover mounted on top of the aerosol inlet should exclude drizzle, rain and snow. Sampling sites that are frequently in cloud or fog, e.g. mountain sites, should use whole-air-inlets to sample cloud or fog droplets. This air should be dried rapidly afterwards to avoid inertial particle losses (see also below).

The sample flow should be laminar in the sample tube to minimize additional losses of small particles due to diffusion and turbulent inertial deposition. The ideal flow should have a Reynolds number of about 2000. An inlet pipe of a diameter of 10 cm yields a flow rate of 150 l/min while an inlet pipe of 20 cm yields a maximum flow rate of 300 l/min. Special care should be given to air splittings, bends and horizontal lines to avoid losses of large particles.

Some components of the inlet system can be built from a variety of materials, but other components require the use of specific materials. The general consideration 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.

Size-dependent Sampling

As discussed in the Introduction, the aerosol mass is usually distributed, between fine and coarse particles with those smaller than about 1 μm being more important for climatic and health effects. The separation of the coarse and fine fractions does not always occur at the same diameter. In marine air, the minimum can be slightly below 1 μm diameter (aerodynamic diameter D_p for unit density spheres) while typical values in more polluted continental air are closer to 2 μm .

The sampling of two size fractions ($D_p < 1\mu\text{m}$, (PM 1) and $1\mu\text{m} < D_p < 10\mu\text{m}$) for mass and chemical analysis is recommended. The separation at $D_p = 1\mu\text{m}$ should be performed with "dry aerosol". Relative humidities between 30-50% are defined as dry (see also the section on relative humidity below). Alternatively, also outdoor samples for mass and chemical analysis can be taken using PM 2.5 inlets with ambient conditions. The size cuts can be accomplished with an impactor or a cyclone; the corresponding device should be characterized. Dichotomous samplers are less suitable due to their flat cutoff curve. If only one size fraction can be analyzed, the submicrometer fraction is preferred.

Special considerations are required at sites that are frequently immersed in clouds or fog. These sites should additionally use an inertial separator to remove particles larger than 10 μm from the dried aerosol. Here, impactors are preferred because of the sharper cut-off curve.

Relative Humidity

A major fraction of the particles in the atmosphere are hygroscopic, and their size can be strongly dependent on the relative humidity. In order to have samples that are size-segregated independent of ambient RH the sample air must be dried to a reference humidity prior to the size segregation step. Fortunately, particle size is relatively insensitive to RH at humidities below 30-50%, so that the air stream does not have to be dried completely. It is recommended that the relative humidity should be controlled to 40% by heating the incoming airstream including the measurement unit. In hot and humid environments dewpoint temperatures in excess of 25°C can be expected, requiring the air to be heated to over 40°C to achieve the desired RH. Under such conditions, significant evaporation of volatile compounds may occur. To prevent this we recommended to use diffusion dryers or a dilution of the sample air with particle-free air. However, the sampling system should be kept as simple as possible for all stations.

If only one size fraction can be taken, it is suggested to sample either at a cut diameter of 1 µm dry or 2.5 µm ambient. For sites with high coarse mode concentrations, sampling of two size fractions is recommended.

Local Contamination

Each site should aim for the best possible control to minimize the effect of local contamination. Site selection must consider avoidance of local sources. Each site may take active measures to avoid local contamination, however, the routine should be simple. These measures should interrupt the filter sampling either by turning off the pumps or by-passing the sample air. As a control mechanism, a combination of wind sector and particle number concentration measurements is suggested. Certain wind sectors with local aerosol sources can be excluded from sampling. Also a rapid rise in particle number concentration ($D_p > 15 \text{ nm}$) can be used as indicator of a local aerosol source.

Time Resolution for Continuous Measurements

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

Quality Assurance and Control

The design of inlets and sampling lines as well as modifications should be co-ordinated with the World Aerosol Calibration Centre.

3.1 Aerosol Mass and Chemistry

Methods of Measurement and Sampling Frequency

As mentioned in the section on General Sampling Considerations, sampling of two size fractions (either 10 µm ambient and 1 µm dry or 10 µm ambient and 2.5 µm ambient) is recommended. The simplest sampling technique is to collect particles on filters. 24-hour samples are recommended. Sampling should be daily, and if not possible then less frequently, e.g. every 6th day, but must be consistent throughout the measurement duration. Different types of samplers and filters may be used, in either low-volume filterpack or high-volume samplers, depending on the specific components to be analyzed. Continuous methods for mass determination such as TEOM or β -meters are also acceptable (although there are known artifacts associated with these methods), with operation conditions clearly stated in sampling logs. During special study periods, size distribution measurements can be done using cascade impactors.

Samples are analyzed for mass and chemical species. In the absence of continuous measurements, mass can be obtained from weight differences of filters before and after sampling. The weighing is to be performed between 40 and 50% relative humidity (RH) with an anti-static electricity device, after an equilibration time of 24 hours.

Chemical analysis should first aim at the major components in order to get a good mass balance. Therefore, major anions and cations should be determined as a first priority, where sampling on teflon filters and analysis by ion chromatography (IC) is recommended. In addition, analysis of total carbon after sampling on quartz filters is recommended in the absence of artifact-free methods for separating organic and elemental carbon. Furthermore, elemental concentrations can be obtained from several analytical procedures such as atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICP-MS), instrumental neutron activation analysis (INAA), and particle-induced X-ray emission spectrometry (PIXE) analysis and X-ray fluorescence (XRF).

QA/QC

Sampling and analytical procedures should be standardized across the entire monitoring network, for which standard operating procedures (SOPs) need to be provided. It is imperative that the monitoring activities be quality assured and the data quality controlled. On a fixed schedule, such as monthly or quarterly, a survey of sample recovery rate for each network station should be maintained which can be used as a basis for corrective actions, if needed. Compliance with the standard operating procedures for sampling and analysis should be documented on the same schedule. A set of compliance criteria must be developed against which the check can be made. These documents should form part of the data together with the results from the sampling/analysis activities. Data delivery to a central depository (such as the World Data Centre for Aerosols, WDCA) should be done at least once yearly.

Quality control for sampling should involve (1) calibration, (2) flagging of data with known abnormalities, and (3) recording these with data. Calibrations of sampling instruments include mass flow measurement calibration with a transfer standard (e.g., a bubble meter or mass flow meter), and leak tests of sampling system should be done at least once a year, and more frequently should problems develop. Analytical procedure quality control should consist of at least three steps: (1) performance check by involving the lab. in interlaboratory intercomparisons, as well as obtaining absolute standards if available, (2) interspersing QC standards with regular samples in a routine analysis sequence, and (3) regularly scheduled repeat analyses of randomly selected 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 the data centre.

Ancillary Measurements

Standard meteorological measurements of temperature, pressure, RH, wind speed, and wind direction are required.

Data Reduction

Data need to be evaluated against the SOPs and the QC procedures, such as sample recovery rate or flags for outliers, before any serious data analysis for scientific information. Statistical tests must be set as a basis to accept or to reject a given data set. For example, a low recovery rate may render a data series useless for a rigorous statistical test of long term trends. Data analysis may be carried out after the data meet such criteria.

Archiving Procedures

After completion of chemical analysis, all data must be recorded using a predefined format on an electronic data system. Mass and chemical components are stored as mass concentrations per volume (e.g., $\mu\text{g}/\text{m}^3$) under standard conditions (which must be specified in the data). Data

that need 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 collection point. A copy of the final product, along with a copy of the SOPs, needs to be submitted to the WDCA.

Application of Results

Data, after evaluation against set criteria, may be used for a number of purposes. For example, the aerosol mass concentration may be used to evaluate the regional PM levels, which may provide information to authorities for potential health risk and exposure on a regional scale. Both mass and chemical data may be used to address questions regarding regional problems of air quality, acid deposition, aerosol-cloud interaction, visibility reduction, and for comparison with simultaneously measured optical parameters.

Longterm trends may be deduced from a continuous and relatively unbroken series of data. Long term reliable record may also be used in the scientific community to verify models that attempt to incorporate aerosols. In addition, reliable data may be used for ground truthing of remote sensing measurements such as satellite-based radiation measurements.

Equipment and Infrastructure Cost (US \$)

Initial capital cost

Low volume sampling system:	4,000
(Alternatively, Hi-vol sampling system:	3,000)
Infrastructure (frame, tower etc):	1,000
Filters:	1,000
Other supplies:	500

Lab Instrumentation

Ion Chromatograph:	65,000
AAS:	40,000
ICP-MS:	110,000
Operating cost per year (no personnel cost):	10,000 (depending on number of analyses)
INAA:	90/sample
PIXE:	50/sample
(both analyses to be conducted at established labs)	

Personnel requirements and training

Personnel:	On-site operator for weekly samples: 3 man-months per year
	Laboratory analyst: 3 man-months per year for each site
	Data analyst/archivist: 3 man-months per year for each site
Training:	On-site operator: training for 1 week
	Laboratory analyst: special analytical chemistry skills required beyond Bachelor of Science degree in analytical chemistry
	Data analyst/archivist: special computer skills required beyond Bachelor of Science degree in computer science.

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Further information on this subject can be found in the EPA report, *Air quality criteria for Particulate Matter*, that can be downloaded from www.epa.gov/ncea/partmatt.htm

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3.2 In-situ Measurements of Aerosol Radiative Properties

Importance

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 (σ_{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 aerosol light scattering (σ_{sp}) and light absorption (σ_{ap}) coefficients.

Methods of Measurement and Sampling Frequency

Aerosol light scattering coefficient is measured with an integrating nephelometer. Simple integrating nephelometers, which operate at a single wavelength, are suitable for air quality and visibility studies. More complicated instruments operate at multiple wavelengths and have the added feature of being able to measure σ_{sp} over two angular ranges: total scattering (7-170° degrees) and hemispheric backscattering (90-170°, denoted as σ_{bsp}). These additional parameters are needed for radiative climate studies. The basic principle of operation of both classes of instruments is the same: a photodetector views a black object through a volume of air, which is illuminated from the side by a light source. Baffles prevent the source from shining on the detector, so that the only light reaching the detector comes from scattering by air and particles in the sample volume. The name "integrating" derives from the internal geometry and illumination, which together perform the properly-weighted angular integration of scattered light needed to measure σ_{sp} . Calibration is performed using gases with known scattering coefficients, with air and CO₂ being the most commonly used.

Aerosol light absorption coefficient is typically determined by measuring the change in light transmission through a filter before and after particles are deposited on the filter. This analysis can be done on the quartz-fiber filters used for analysis of carbonaceous species (see chapter on mass and chemistry). At some sites, it may be desirable to determine the light absorption coefficient with a higher time resolution than the filter samples allow. 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 fiber 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.

Both of these measurement techniques operate continuously, and 1-minute time resolution is readily achievable in all but the cleanest locations. Such high time resolution is impractical for monitoring applications, where hourly or even daily averages are more appropriate.

QA/QC

Quality assurance begins with proper operating procedures. Supermicrometer particles should periodically be excluded from the sample stream, in order to allow determination of the size dependence of aerosol optical properties. The cut size should be the same as is used for the aerosol chemical sampling system, to allow determination of the mass scattering and absorption efficiencies. Comparison of results from different locations is facilitated by choosing a common reference humidity for operating the instruments; a value of ~40% is recommended. Routine measurements of the nephelometer calibration gases are desirable, in order to quantify the uncertainty of the measurements and to detect changes in instrument performance. Correction factors for the effects of instrumental non-idealities should be applied, as described in *Anderson and Ogren* [1998] and *Bond et al.* [1999]. The nephelometer correction factors are much larger for supermicrometer particles than for submicrometer particles, which is another reason to make size-segregated measurements.

Routine maintenance for these instruments is minimal. The filter in continuous light absorption photometers should be changed when the light transmission drops below ~70% of its initial value - in polluted locations, this could be several times per day. Lamps and internal filters may need to be changed once or twice a year, depending on the instrument and operating environment. 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. System integrity should be checked monthly, by placing a filter on the system sample inlet and measuring the pressure drop and CN concentration downstream of the samplers. This simple check will quickly reveal any leaks that might have developed in the system.

The key to identifying the need for maintenance is to keep 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. The calibration of flowmeters and ancillary sensors should be checked on an annual basis.

Ancillary Measurements

The aerosol light scattering coefficient 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. It is imperative that the RH in the sample volume be measured continuously and reported along with the scattering data. 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.

Data Reduction

Modern, computer-controlled instruments provide data that have already been converted to physical units, so very little post-processing is needed. Adjustments due to calibration drift might be needed, local pollution events should be removed or flagged, and corrections for instrument non-idealities should be applied.

Archiving Procedures

The GAW archive for aerosol data is the World Data Centre for Aerosols (WDCA) located at the Joint Research Centre (JRC), Ispra, Italy (EU).

Application of Results

Scattering and absorption by particles reduce the transmission of light through the atmosphere, causing effects on radiative climate and visibility. Measurements of aerosol radiative properties are used to evaluate the magnitude of these effects, and, when combined with simultaneous measurements of aerosol chemical composition, allow attribution of the effects to different chemical species or source categories. Moreover, the aerosol light scattering coefficient has been shown to be highly correlated with PM_{2.5} mass concentration, and integrating nephelometers can be used to provide estimates of PM_{2.5} mass concentration where high time resolution is required.

Equipment and Infrastructure Costs (US \$)

Integrating nephelometer:	5,000 - 60,000
Light absorption photometer:	5,000 - 20,000
Infrastructure:	5,000 - 20,000

Personnel Requirements and Training

Undergraduate training in a physical science or engineering is desirable for technicians operating the instrumentation described here. These instruments require minimal attention (< 30 minutes) on a daily basis for operating checks and filter changes.

References

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3.3 Condensation Nuclei

Importance

Condensation nucleus (CN) concentration represents a single integral measurement of particle number across a wide size range, encompassing several modes in the particle size distribution. The recommended standard measurement for GAW is the concentration of particles with diameter $D_p > 12$ nm (N_{12}) or $D_p > 10$ nm (N_{10}), with more comprehensive programmes also measuring $D_p > 3$ nm (N_3). CN concentration gives an overall indication of the balance between fine particle production and removal in the sampled region and hence will be responsive to long term changes in these processes.

Numerous epidemiological studies suggest a link between the mass of fine airborne particles and human health (see for example Dockery and Pope 1996). The concentration of ultra-fine particles (in this context defined as particles with $D < 100$ nm) is also considered a possible factor in the adverse impact of airborne particles and human health (Obersdorfer et al. 1995, Seaton et al., 1995). In urban and rural air, CN number concentration often represents a good indicator for this size fraction.

As high number concentrations of CN are produced mainly by anthropogenic activities, particularly combustion processes, CN can be used for active control of other aerosol sampling devices such as filter collectors. In this case large concentrations or rapid increases in concentration of CN are an indicator for local sources that might otherwise be disproportionately represented in the collected sample.

Methods of Measurement and Sampling Frequency

Condensation nuclei are atmospheric particles detected after condensation of water or other condensable vapor, often an alcohol such as butanol, from a supersaturated atmosphere onto the particle. Counters are known as condensation particle counters (CPCs) or condensation nucleus counters (CNCs). Continuous sampling is preferable, with raw data representing integrals over 1 to 3-minute periods.

QA/QC

One basic quality assurance strategy is to use two counters, preferably with real-time graphic display of the output concentration record. Other measures at the observatory include keeping instrument maintenance and operating logs, regular calibration of flow rates (every 1-3 months) and count zeros. An annual comparison with an independent counter as part of a network-wide GAW QA plan is recommended. At the data reduction level, an independent observer should review operating logs and the data should be reviewed independently, bad data must be flagged.

For the full QA plan see the GAW operating manuals.

Data reduction

Raw data may be either particle counts over a time period or particle concentration, depending on the instrumentation employed. If the raw data are counts they need to be reduced to concentrations using the measured sample flow rate. The time resolution of the raw data should allow generation of hourly statistics, which should include arithmetic mean and standard deviation, median, minimum and maximum CN concentration for each hour. Bad data should be identified and flagged.

Archiving Procedures

Reduced data to be submitted to World Data Centre for Aerosols (WDCA) at the Joint Research Centre in Ispra, Italy, (EU).

Application of Results

CN number concentration is an indicator of the regional balance between particle production and loss processes and changes in overall particle concentration with time. One principal application is in validation global aerosol climatologies, where the integral property of CN is a constraint on particle size distribution. CN are also useful for characterizing air masses and as indicators of local pollution (see section on General Sampling Considerations). Particle number is receiving increasing interest in epidemiological studies on human health.

Equipment and Infrastructure Costs (US \$)

N₁₀, TSI 3010, 20,000
N₁₂, TSI 3760A, 15,000
N₁₂, TSI 3762, 16,000
N₃, TSI 3025A, 38,000
N₇, TSI 3022A, 32,000

Running costs: low

Personnel Requirements and Training:

Operator: trained technician, about 1 hour per week
Training: 1 day

References

Dockery D. and A. Pope, Epidemiology of acute health effects: Summary of time series studies. In *Particles in Our Air: Concentrations and Health Effects*, R. Wilson and J. Spengler, eds., Harvard University Press, pp. 123-148, 1996.
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3.4 Cloud Condensation Nuclei

Importance

Cloud Condensation Nuclei (CCN) measurements are made to establish climatologies of those particles that have the potential to produce cloud droplets at supersaturations less than about 1%, that is in conditions typical of natural clouds. Climate forcing by indirect effects of aerosol on clouds represents the single largest source of uncertainty in climate models (IPCC 1996).

Siting requirements

CCN measurements are recommended only at GAW global sites with well-established aerosol programmes. CCN measurements can be made on air sampled from a main instrument housing sampling-stack that has minimal particle losses. Pre-conditioning of the sample stream is not required and any size-selective stages should be bypassed.

Methods of Measurement and Sampling Frequency

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 commercial instruments or purpose-built instruments is necessary. Past CCN measurements in the GAW programme have predominantly used static thermal-gradient chambers. These are well

suited to relatively low-frequency sampling and low-resolution (differential) CCN spectrum determination. Instruments utilizing continuous flow offer some advantages, but have yet to be implemented in GAW for more than single “process studies”. Measurement methods that have available droplet growth times comparable to real clouds are preferable.

Measurements may be made at a fixed supersaturation, 0.5% is suggested, or may involve collection of CCN spectra (concentration as a function of supersaturation).

QA/QC

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. Other measures at the observatory include keeping instrument maintenance and operating logs, regular calibration of flow rates (1-3 month) and count zeros for continuous flow instruments. Annual comparison with an independent counter as part of a network-wide GAW QA plan is recommended. At the data reduction level, an independent observer should review logs and the data should be reviewed independently, bad data must be flagged.

For a full QA plan see the GAW operating manuals.

Data Reduction

Fixed supersaturation. The time resolution of the raw concentration data should allow generation of hourly statistics, which should include arithmetic mean and standard deviation, median, minimum and maximum CN concentration for each hour. Bad data should be identified and flagged.

Spectra CCN spectrum data may be recorded either as differential data, comprising CCN concentration as a function of supersaturation or cumulative concentrations as a function of supersaturation.

Archiving Procedures

Reduced data should be submitted to the World Data Centre for Aerosols (WDCA) at JRC, Ispra, Italy (EU).

Application of Results

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.

Equipment and Infrastructure Costs (US \$)

No commercial instruments known

Running costs: low

Personnel Requirements and Training

Operator: trained technician, about 1-2 hours per week

Training: 1 day

References

IPCC (1996), Climate Change 1995- The Science of Climate Change, Cambridge University Press, the University of Cambridge, The Pitt Building, Trumpington St., Cambridge CB2 1RP, UK. Eds. J.T Houghton, L.G. Meira Filho, B.A. Callander, N. Harris, A. Kattenberg and K. Maskell.

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3.5 Aerosol Optical Depth

Method of Measurement and Sampling Frequency

Aerosol Optical Depth (AOD) is determined from the measurement of spectral extinction of solar radiation in the atmosphere. The solar irradiance I at a given wavelength can be expressed as $I = I_0 \exp(-m\tau)$ with I_0 the extraterrestrial (outside-the-atmosphere) irradiance of the sun, m the airmass and τ the total optical depth. The airmass 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 τ at a given wavelength is composed of τ_i from several sources, such as from scattering at gas molecules, τ_R (Rayleigh scattering), extinction by aerosol particles, τ_A , and absorption of trace gases, τ_G , by e.g. ozone. As we are interested in aerosol optical depth we have to subtract from the observed τ the other components; thus, $\tau_A = \tau - \tau_R - \tau_G$, which includes scattering and absorption of the aerosol. From the knowledge of I_0 , m , τ_R , τ_G the aerosol optical depth can be calculated for the wavelength of observation.

Such measurements can be performed with a variety of instruments, such as sunphotometers, rotating shadowband filterradiometers or spectroradiometers. The most common instruments are sunphotometers which should more correctly be called filterradiometers (FR), as their wavelengths are not limited to the visual (photometric) spectral range. WMO recommends three centre wavelengths at 368, 500 and 862 nm, with an optional channel at 412 nm and a bandwidth of 5 nm. For FR and rotating shadowband radiometers interference filters are used to select the wavelength and silicon diodes as detectors.

In a first attempt to establish a world AOD climatology the BAPMoN programme was established with hand-held sunphotometers with 10 nm bandwidth filters at 380 and 500 nm. A detailed examination of the results of this network revealed serious flaws in both the internal consistency of data from individual stations and the comparability between stations. Thus, these measurements were terminated in 1993. New instrumentation was developed in the mean time and several products are available commercially. In addition, a Swiss initiative, started in 1996, resulted in the development of precision filterradiometers (PFR) with 4 channels which are being tested in a trial phase at 12 GAW Global observatories. The objective is to demonstrate that the new generation of instruments together with new calibration techniques and quality assurance procedures is indeed able to determine AOD with a precision adequate for the fulfillment of the objectives of GAW.

From the experience with hand-held instruments it became clear that besides instrumental improvements the operational procedures have also to be refined. It became also obvious that the precision can only be achieved with quasi-continuous measurements by a FR on an automatic tracker system, and with an accurate digital data acquisition system. This guarantees accurate

aiming at the sun and, more importantly, allows measurements with accurate timing at a frequency of 2-5 minutes permitting effective quality assurance procedures to be applied.

Calibration

As stated above, the determination of AOD needs knowledge of I_0 which is often referred to as the calibration of a FR or similar instrument. In principle this value, which is normally given in units of the instrument output (e.g. volt), can be determined by the Langley method which is based on $I = I_0 \exp(-m\tau)$ or $\log(I/I_0) = -m\tau$, that is by extrapolating the measurements at different m to $m=0$ and I_0 . Obviously this yields reliable results only if τ is constant during the measurements. Thus, such a calibration can only be performed with sufficient reliability from high altitude stations during clear days. Even with the best conditions the day-to-day precision is about one percent and thus another method has to be used to check the stability of the instrument. For this only highly accurate absolute calibration methods are adequate, such as detector based methods using a cryogenic radiometer as the basic standard. For the PFR calibration such a method has been developed at the World Optical depth Research and Calibration Centre (WORCC) at PMOD/WRC Davos, which is responsible for the calibration of the AOD measurements within GAW. First results of the calibration procedures can be found in Wehrli (2000). The extraterrestrial irradiance, however, is not known with an accuracy similar to the one achieved in the laboratory and thus we still have to rely on Langley extrapolations. These can, however, only be performed at well selected stations and certainly not at all stations where FRs are operated. As a consequence, the calibration is periodically transferred with a traveling standard to the stations where side-by-side comparisons are performed. In the case of the 12 GAW Global observatories which have all the same type PFR this is rather straightforward; for the other stations with FR with slightly different wavelengths the calibration procedures have still to be developed. Moreover, these procedures have then to be implemented with the help of, e.g., regional radiation centres, as WORCC cannot perform all these tasks.

Ancillary Measurements

As stated in the first section the Rayleigh optical depth above the station is required, which can be calculated from the station pressure. Moreover, the 500 nm channel is influenced by ozone, so its column density has to be known. A nearby Dobson station may provide the data or some adequate device at the station itself.

Data Reduction

For each measurement the Sun-Earth distance and the solar zenith angle are needed, which can be calculated by astronomical programmes with sufficient accuracy. With I_0 , provided by the calibration facility (for the PFR at the Global Observatories from WORCC, for the regional stations from a calibration centre with standards traceable to WORCC), and the solar zenith angle the relevant airmasses and optical depths can then be calculated, including the final result, the AOD. Corresponding algorithms and programmes are under development and will be made available from WORCC.

Archiving Procedures

Although the AOD is calculated at the station, mainly to enable a first quality control, the raw and the evaluated data will be archived together with an instrument history, including results from initial and periodic calibrations. Some *a posteriori* corrections may be needed which can be applied only later (e.g. adjustments for calibration drifts). Corresponding data formats are defined and available from WORCC. The data are finally archived at the World Data Centre for Aerosols (WDCA) at JRC, Ispra, Italy (EU).

Application of Results

A global AOD climatology is very important for the assessment of the influence of aerosols on climate and global change and has not - even partly - been established yet. Moreover, many remote sensing applications from satellites depend on a normally unknown aerosol content. Over oceans the AOD may be determined from radiance measurements from satellite, but over land this is impossible and only accurate measurements from ground can provide the necessary data sets. Measurements from isolated islands may help with ground truth to test satellite remote sensing devices and algorithms.

Equipment and Infrastructure

There are not many possibilities to get accurate FR instruments commercially. Below a selection of 3 instruments which have a proven design are given; the list is, however, not complete. Within the tasks of WORCC a new type of PFR for 12 GAW Global observatories has been developed which can be purchased from PMOD/WRC¹. The PFR has 4 channels for AOD determination at 368, 412, 500 and 862 nm (about US \$13,000). It comes with a data acquisition system, but without an automatic tracker which has to be provided separately. Another instrument which is used in the Aeronet Programme is a FR from CIMEL², with 8 channels, 4 of which are for AOD determination (440, 870, 670, 1020 nm at about US \$16,000; with the WMO recommended wavelengths it would cost about US \$4,000 more). It comes with a data acquisition and control unit and is mounted on a tracker. A third choice is a multi-filter rotating shadowband (MFRS) radiometer manufactured by YES³ which comes with a data acquisition and control unit and does not need a tracker (about US \$18,000). All 3 instruments need a PC to read the data that are stored in the units for several days.

Personnel Requirements and Training

A technician is needed who is trained for performing and maintaining meteorological radiation measurements. The workload is about 30 min daily, plus 45 min every second or third day and plus 3 hrs once a week. The daily tasks can be also be performed by station maintenance personnel, the others need the technician mentioned above.

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³Yankee Environmental Systems, Inc., 101 Industrial Boulevard, POB 746, Turners Fall, MA 01376, U.S.A., Fax: +1 413 863 0255

3.6 Aerosol Lidar

Importance

A ground-based aerosol programme cannot address all of the important aerosol effects on the atmosphere. For many effects, e.g., for radiative transfer calculations, altitude-resolved information about aerosols is needed. Ground-based remote sensing by lidar (light detection and ranging) can provide the needed information on vertical aerosol distributions and their variations, as well as information on the presence and vertical distribution of clouds.

Siting Requirements

Lidar systems should provide information on the vertical aerosol distribution at GAW sites where an aerosol programme has been implemented. The integration of an aerosol lidar with measurements by radiosonde, ozonesonde and sunphotometer and with trajectory calculations is the most promising combination.

Method of Measurement

An aerosol backscatter lidar system typically consists of a laser transmitter and an optical receiver in parallel or collinear arrangement. The laser transmits intense, short-duration light pulses with high repetition rate into the receiver field of view. The intensity of the light elastically backscattered by atmospheric 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.

To bring the minimum height for measurements down close to ground one can add a low-altitude, wide field-of-view channel, or add scanning in elevation angle to near horizontal. In the 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 down to the station.

The elastic backscatter signal is the sum of backscatter from atmospheric molecules and backscatter from atmospheric particles, and might be influenced by wavelength dependent absorption features of trace gases. The primary data products are profiles of aerosol backscatter, mixed-layer height, aerosol layers in the free troposphere, cloud base height, detection of both visible and subvisible cirrus, and detection (night-time) of stratospheric aerosol after major volcanic eruptions. Secondary products are aerosol extinction profiles and optical depth. A lidar system can also include measurement of depolarization ratio, which provides information on how much the particles deviate from spherical shape. Discrimination between ice and water clouds is the most common application, but depolarization also provides information on aerosol particle shapes.

Data Reduction

Raw intensity data of the backscatter signal will be corrected for background light and range, and then adjusted to account for the two-way molecular and aerosol extinction. The aerosol signal must be separated from the molecular signal by suitable algorithms. A further step is converting the aerosol backscatter profile into an aerosol extinction profile using appropriate internal or external information and algorithms.

Ancillary Measurements

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.

QA/QC

Instrumentation: Similar instrumentation at the various sites

Measurement: Transportable system, blind intercomparison

Retrieval algorithms: Same data retrieval algorithms at all sites; 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 sites or airborne systems.

Archiving Procedures

The data should be sent to the World Data Centre for Aerosols (WDCA) in Ispra, even though no archiving system has been established for tropospheric lidar data so far.

Applications of Results

Lidar observations of the spatial distribution of aerosols allow an understanding of their variation in time, their optical and physical properties, and their influence on cloud formation. The lidar information contributes to determining sources, transport and sinks of pollution, to observation and interpretation of long-term trends, and to predicting climate change.

Equipment and Infrastructure Cost

Lidar systems meeting the requirements of a GAW station are not yet commercially produced, but the technology is now available.

Personnel Requirements and Training

Personnel:

System checks and maintenance: technician

Data evaluation and calibration, data interpretation, quality assurance and control: scientist.

Training:

Technician: field operation - 1 week training; equipment maintenance - 2 weeks training;

Scientist: appropriate education and experience.

References

Relevant general and specific information can be found in the presentations made at the 18th and 19th International Laser Radar Conference (ILRC), respectively, which are published as:

Advances in Atmospheric Remote Sensing with Lidar, A. Ansmann, R. Neuber, P. Rairoux, and U. Wandinger (Eds.), Selected papers of the 18th International Laser Radar Conference (ILRC), Berlin, 22-26 July 1996, Springer, 1997.

Nineteenth International Laser Radar Conference, U.N. Singh, S. Ismail and G.K. Schwemmer (eds.), Annapolis, Maryland, 6-10 July 1998, ASA/CP-1998-207671/PT1, 1998.

Further useful information can be found in the International Lidar Researchers Directory under <http://www-arb.larc.nasa.gov/lidar/directory.html>.

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4. ATMOSPHERIC DEPOSITION

4.1 Wet Deposition

Importance

Measurements of the chemistry of precipitation have been made in many parts of the world beginning over one hundred years ago. In recent years, interest in total deposition (wet plus dry) has increased because of such phenomena as the long range transport of nutrients, acids, and toxic materials. Dry deposition, the settling and impaction of both aerosols and gases to a surface, requires a separate measuring system. (See Section 4.2). Chemical components also deposit to the earth's surface by wet deposition and are analyzed from rain water samples. This is considered precipitation chemistry.

From a broader prospective, wet deposition measurements provide information on the exchange of chemical components between the atmosphere and the land/oceans and hence are an important link in understanding the chemical cycles of such substances as sulfur, nitrogen, and trace contaminants. Changes in these cycles have direct influence on issues ranging from regional air quality to climate.

Siting Requirements

GAW stations collecting samples for precipitation chemistry analysis can be classified as characterizing global or regional conditions. Typically classification depends on a number of factors which include distance from natural and anthropogenic emission sources, location within a given climatological/ecological region, and areal representativeness of the station. Particular care must be taken to avoid dust and other forms of local contamination to prevent compromising the usefulness of the measurements.

Major on-site precautions should be taken to avoid placing the collector near high structures such as buildings and trees. Good sites are typically located on a level grass-covered plot with no obstructions within a minimum forty five degree cone around the collector orifice.

Methods of Measurement and Sampling Frequency

Precipitation chemistry monitoring can be divided into two phases: collection of the sample and laboratory analysis. When a rain or snow event takes place at a site, usually a special open-close collector is activated to capture the sample, or, alternatively, the lid is removed from the funnel of a manual collector. The sample collector is exposed only during periods of precipitation for wet-only sampling. The amount of rain from the precipitation gauge is recorded following the event. Sampling periods are either weekly or daily; longer periods are to be avoided. From past monitoring experience, daily sampling, where the collector is checked at a set time each day, has been found to be the most scientifically useful because samples can be chilled or chemically preserved quickly, preventing significant biological degradation of labile species. Daily samples also are simpler to manipulate in source-receptor modeling exercises. Under the weekly protocol, all events can be composited over a seven day period, a practice that may compromise the utility of some ions, but will clearly reduce programme costs. In some networks, pH and conductivity are determined on site as part of the quality control programme. Samples may be preserved through refrigeration or with the addition of a biocide (e.g., chloroform or thymol) prior to shipment to the laboratory.

The analysis phase begins when the sample is received by the national laboratory or central analyzing facility designated by the WMO. At these laboratories, the major ions are determined (SO_4 , Cl , NO_3 , $\text{H}(\text{pH})$, Ca , Mg , Na , NH_4 , and K). Organic acids such as formic and acetic acids are an important source of free acidity in pristine areas and should be measured at background stations. Conductivity may also be measured as part of a comprehensive quality assurance programme. A wide variety of analysis techniques are used by the different

laboratories, although ion chromatography (IC), atomic absorption spectrophotometry (AAS), and automated colorimetry tend to be the preferred analysis techniques. Bench top chemical analysis techniques should be avoided.

Considerable effort has been made by the WMO to improve the quality of the chemical analyses by conducting annual laboratory intercomparisons. Participating national laboratories analyze a series of test solutions and report the values to the WMO. Test results are compared against the known concentrations and used as a measure of the performance of the given laboratory. Beginning in 2000, laboratory intercomparisons will be conducted twice annually.

Data Reduction and Archiving Procedures

After completion of the laboratory analyses, a number of quality assurance checks are performed including ion balances and conductivity checks. Outliers are identified, data records are carefully examined, suspect samples are re-analyzed, and questionable samples are flagged in the database. When all quality checks have been made, the data are sent to the World Data Centre for Precipitation Chemistry (WDCPC) for additional quality assurance and archival. At the present time the WDCPC is collocated with the Quality Assurance/Science Activity Centre for the Americas; at State University of New York in Albany, New York.

Application of Results

Scientists have actively used the precipitation chemistry data from GAW along with other data sets from major world networks to investigate a number of environmental problems. Historically, main areas of use have included impact studies of acid rain on the environment, the establishment of trends in sulfur and nitrogen deposition, and as validation for model calculations of pollutant transport. More recently, the data have been used to determine nutrient deposition to threatened ecosystems such as coastal estuaries and poorly buffered freshwater systems, and to determine effectiveness of emissions reductions regulations, particularly for sulfur.

Equipment and Infrastructure Cost (US\$)

Field Collection

Open-close collector	- 2000 to 12,000
National rain gauge	- 2000 to 10,000
Postage, plasticware etc.	- dependent on location of laboratory relative to field station
pH meter (optional) with buffers	- 1000
Conductivity meter (optional)	- 500
Laboratory Analysis (per sample)	- 35 to 100 depending on the ion suite, rigor of quality assurance programme and whether or not data archival and data dissemination tasks are included.

Personnel Requirements and Training

Training:	Site operator: less than one week should be sufficient for comprehensive training. Analytical laboratory: a well trained laboratory technician is required and a chemist for data evaluation.
Personnel:	The time required for the site operator depends on frequency of sampling: Weekly - one man month per year Daily - three man months per year

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Bowersox, V.C., M.E. Peden, K.O.W. James: Quality Assurance Plan, NADP/NTN Central Analytical Laboratory (CAL), National Atmospheric Deposition Programme, Illinois State Water Survey, Champaign, IL 61820, July 1993.

Dossett, S.R., and V.C. Bowersox: National Trends Network Site Operation Manual, Programme Office, National Atmospheric Deposition Programme, Illinois State Water Survey, Champaign, IL 61820, July 1999.

EMEP(1995) EMEP Manual for Sampling and Chemical Analysis, Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 1/95).

Environment Canada, Canadian Air and Precipitation Monitoring Network, Laboratory Standard Operating Procedures Manual, Volume I, Precipitation Methods (December, 1994).

WMO, in preparation: Guidance Document on Precipitation Chemistry Measurements.

Web Pages:

Publications, report updates, manuals, and meetings are often reported on the following web pages:

<http://marble.asrc.cestm.albany.edu/qasac/>

<http://airquality.tor.ec.gc.ca/natchem/>

<http://nadp.sws.uiuc.edu>

<http://www.nilu.no/projects/ccc/>

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4.2. Dry Deposition

Importance

The term "dry deposition" commonly refers to any atmosphere-surface chemical exchange that occurs other than during precipitation events. It is most commonly thought of as a downward transfer, but this notion can be misleading because some chemicals undergo a bi-directional exchange between the atmosphere and the underlying surface. Air-surface exchange is a complex process whose rate is determined by a variety of factors, including atmospheric turbulence and stratification; the chemical and physical characteristics of the deposited compound; the presence and extent of a chemical gradient between the atmosphere and receptor surface; and the chemical, physical (height, surface area, etc.), and biological characteristics of the receptor surfaces.

Dry deposition is a slow but continuous flux of airborne contaminants to or from an underlying surface. It contrasts greatly to wet deposition, which is a rapid delivery of highly concentrated pollutants during precipitation events. Moreover, dry deposition necessarily involves pollutants carried in the lowest layers of the atmosphere, in air that is in contact with the surface. The importance of dry deposition in most areas of the world has never been well documented. Dry deposition is generally far more a local problem than wet. However, in highly industrialized areas, its regional importance is also thought to be great because of the large number of emission sources. In parts of the eastern United States, central Europe and eastern Asia, and in regions with little precipitation, dry deposition is likely to be at least as important as wet.

Siting Requirements

For common sampling methodologies, siting requirements typically exceed the requirements for a properly sited precipitation chemistry station. The most representative stations are located in broad areas of continuous fetch of a single species of vegetation, away from tall objects, edges of forests or bodies of water. Forest sites are also acceptable, provided that the forest stand is fairly uniform in species composition and height, and of sufficient area to avoid edge effects.

Methods of Measurement and Sampling Frequency

There are many methods available to estimate dry deposition at a point. Two common approaches are discussed here: eddy flux measurements, and dry deposition inferential monitoring (DDIM). Other methods such as eddy accumulation, throughfall/stemflow techniques and snowpack accumulation are not discussed.

Eddy flux or eddy correlation measurements are available for certain key pollutants (e.g., SO₂, O₃, and NO_x) and some trace gases (e.g., CO₂). They provide direct measurements for comparison to filterpack-based estimates made using fast and slow-response meteorological equipment and fast-response (> 1 Hz) chemical sensors.

DDIM stations make use of current generation data loggers and mean measurements of meteorological variables, and rely on filterpacks and regulated flows for time-integrated concentration sampling. Meteorological data are typically averaged over periods of thirty or sixty minutes; filterpacks are replaced at least weekly.

Data Reduction

Using the eddy correlation method, wind fluctuations in the vertical and chemical concentration fluctuations are determined in real-time, and the flux (related to the product of these quantities) is measured directly. Deposition velocities are calculated by dividing the measured chemical flux by the measured concentration.

DDIM meteorological data are typically averaged on-site by a data logger and then used in a mathematical model of the transfer process to estimate a deposition velocity. Filterpack chemical data are analyzed in a laboratory, typically using equipment also appropriate for precipitation chemistry analysis. (See Section 4.1) Flux values are then calculated as the product of the estimated deposition velocity and the measured concentration.

Archiving Procedures

DDIM and eddy correlation data are not formally archived at this time. However, DDIM and similar monitoring data for North America have been collected into the Canadian National Atmospheric Chemistry (NatChem) Database and Analysis System, and are being quality checked prior to posting on the Internet. This is a work in progress. The URL for dry deposition-related data is <http://arqm.tor.ec.gc.ca/netchem>. Eddy correlation data are generally available only from individual researchers.

Application of Results

Dry deposition measurements are crucial to the estimation of total deposition and critical loads anywhere that dry deposition is important. Dry deposition measurements also provide a critical parameter for mass balance calculations, especially for nutrient cycling studies involving closed or poorly circulating water bodies. Many dry deposition concerns involving heavy metals (e.g., Hg) are beginning to emerge, as chemical measurements improve and links to human health are discovered.

Equipment and Infrastructure Cost (in US\$)

DDIM System	
Equipment	5,500
Laboratory analysis (annual)	10,000
Eddy Flux System	
Equipment	200,000
Annual Maintenance	20,000

Technician (1/4 time)
Scientist (1/4 time)

Personnel Requirements and Training

Routine operation of DDIM stations typically require about as much time and a similar level of expertise as the operation of a precipitation chemistry station, usually about an hour or two, once per week. Operator training could easily be accomplished in one week for a DDIM system. Data sampling and meteorological equipment problems generally require the aid of more skilled technicians. Eddy flux devices, while greatly improved in the last several years, still require about one-fourth of the time of both a trained scientist and an experienced technician or engineer.

References

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5. RADIOACTIVE SUBSTANCES

5.1 Radon-222

Importance

Radon-222 (^{222}Rn) is an inert gas resulting from the alpha decay of radium in the uranium-238 decay chain, with a half life of 3.82 days. Because ^{222}Rn fluxes from soils are typically 100 times that from the ocean, ^{222}Rn is useful as a tracer for air masses which have recently passed over land. Studies at the Mauna Loa Observatory in Hawaii have identified diurnal episodes of ^{222}Rn transported from local sources, and the long term transport of air from distant continents. In conjunction with other radionuclide measurements, such as ^{210}Pb , ^{222}Rn data provides a useful constraint in evaluating air transport models and in identifying global atmospheric conditions.

Siting Requirements

Because of its short residence time in the atmosphere and wide range of surface emanation rates, the interpretation of ^{222}Rn measurements is highly site-specific. Radon-222 has been routinely measured at both continental and remote global sites. Long range transport studies are best made from coastal or high-altitude sites free of local ^{222}Rn sources.

Methods of Measurement and Sampling Frequency

In a typical ^{222}Rn monitoring instrument, air is drawn through a filter that removes all the ambient progeny but allows the inert ^{222}Rn gas to pass. The ^{222}Rn then flows through a large decay-chamber that allows the ^{222}Rn gas to decay and produce new progeny (^{218}Po with half-life of 3.05 min). These are collected on a second filter, and their alpha activity is measured by a scintillation detector.

The sensitivity of the instrument is principally dependent on the volume of the decay-chamber, but a number of other factors such as the flow rate, chamber geometry, progeny capture efficiency, sampling interval, and counter efficiency also influence performance. For example, the ^{222}Rn counter at the Cape Grim Global Station had a detection limit of 0.05 Bq/m^3 for sampling/analysis intervals of 30 minutes, which is equivalent to the typical ^{222}Rn concentrations in oceanic air. The usual frequency for sampling is 1-2 samples per hour. The Environmental Measurements Laboratory's (EML) 500 liter decay-volume instruments have a sensitivity of 130 counts for a 1 hour sample and 1 hour count for a ^{222}Rn concentration of 0.37 Bq/m^3 . The background of these instruments is less than 8 counts/hr. For measurements of ultra low concentrations at high altitude, EML's Radgrabber instrument designed for aircraft measurements of ^{222}Rn produces, in real time, 1 count/min of ^{218}Po at the small concentrations of 0.037 Bq/m^3 .

Data Reduction

Data are collected and stored by a dedicated processor and saved to a floppy disk. The data stream includes several environmental and housekeeping parameters as well as raw counts. The data are edited and ^{222}Rn concentrations are calculated.

Archiving Procedures

The ^{222}Rn data are archived at the WMO World Data Centre for Greenhouse Gases, operated by the Japan Meteorological Agency in Tokyo.

Application of Results

Radon-222 data can be used in monitoring continental airmass events. The enhanced ^{222}Rn concentrations at an oceanfront station could announce the arrival of air that had recently passed over land. The large concentration difference of measured ^{222}Rn between continental and

maritime air provides a further means to validate synoptic scale horizontal transport. The ^{222}Rn data is an ideal tracer for studying atmospheric mixing processes in the troposphere.

Equipment and Infrastructure Cost

No commercial radon measuring device is presently available. A dual filter monitoring device may cost about US \$10,000 to \$15,000 to construct.

Personnel Requirements and Training

Personnel: Operation and calibration of ^{222}Rn monitor - 8 hours per month

Data reduction, archival, dissemination - 24 hours per month

Training: Radon-222 monitor operations and calibration - one week

References

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5.2 Krypton-85

Importance

Krypton-85 (^{85}Kr) is a radioactive noble gas which decays with a half-life of 10.76 years, emitting mainly β -particles of mean energy 251 keV. The main sources of ^{85}Kr are the nuclear fuel reprocessing plants and various nuclear reactors. The nuclear weapons tests in 1945-1963 contributed about 5% of the total ^{85}Kr in the atmosphere, whereas its natural sources can be neglected. Radioactive decay is practically the only mechanism of ^{85}Kr removal from the atmosphere. The present background concentrations of ^{85}Kr in the atmosphere are about 1 Bq/m^3 and are doubling every 20 years. At this level, ^{85}Kr is not dangerous for human beings, but the air ionization caused by ^{85}Kr decay will affect atmospheric electric properties. If ^{85}Kr continues to increase, changes in such atmospheric processes and properties as atmospheric electric conductivity, ion current, the Earth's magnetic field, formation of cloud condensation nuclei and

aerosols, and frequency of lightning may result and thus disturb the Earth's heat balance and precipitation patterns. These ^{85}Kr -induced consequences call for ^{85}Kr monitoring. In addition, because of the well-known sources and sinks of ^{85}Kr and its chemical stability it is a good tracer for testing the global tropospheric transport models.

Siting Requirements

For background determination, the current GAW global stations such as Mauna Loa, Cape Grim, the South Pole, or almost any other location remote from ^{85}Kr sources can establish the global pattern. But if one wishes to use the emissions of ^{85}Kr for transport and diffusion studies, as have been reported downwind of the Idaho Falls and Savannah River nuclear installations, then additional locations in the downwind (and for background, upwind) sectors of the source would be needed. ^{85}Kr being a noble gas, the special precautions that must be applied to other gases at background stations can be disregarded; natural ^{85}Kr sources or interferences are either absent or can be easily dealt with.

Methods of Measurement and Sampling Frequency

Although there are several methods for collecting krypton from the atmosphere, the most usual and practical ones are cryogenic, using a charcoal trap immersed in liquid nitrogen. Before sampling, carbon dioxide and water vapor should be removed from the air. However, the aliquot so collected must be subsequently purified in a central laboratory by additional absorption and chromatographic separation. The elimination of radon, also radioactive, is especially important. Counting the radioactivity relative to a standard ^{85}Kr sample is normally accomplished in a Geiger-Mueller tube or by a scintillation gas radiometer. To date, there have been no or few intercomparisons of standard gases and none are commercially available through national standards laboratories. Current background concentrations in the atmosphere can be measured to a precision less than several percent relative to a standard ^{85}Kr gas at a competent radiochemical laboratory. Taking into account the mixing time of trace substances during the long-range transport, the frequency of ^{85}Kr sampling at background stations should be once every 1-2 weeks.

Data Reduction

Data reduction presents few problems at the radiochemical laboratory. Normally, the laboratory aliquot being counted for its radioactivity after purification represents a sample of krypton, not whole air. The original amount of whole air from which it was derived is known too imperfectly to be useful. Usually there is no or negligible fractionation of isotopes among the krypton isotopes during the collection and purification; the concentration of ^{85}Kr per unit volume or mass of air at a given pressure and temperature can be calculated if the average abundance of krypton in the atmosphere, about 1.14 ppm, is used.

Archiving Procedures

To evaluate the reliability of data for application to geophysical or biological problems, a measure of the uncertainty in the reported numbers must be given. This may include other information than only the measured or estimated uncertainty. The additional information might be the values of the several counts of the sample if more than one was made, the amount of krypton gas available for counting, the background of the counter, etc. The krypton-85 data are collected at the WMO Data Centre for Greenhouse Gases, operated by the Japan Meteorological Agency in Tokyo.

Application of Results

The application of the results will be those described under Importance. In addition, many scientists will be interested in the growth of ^{85}Kr in the atmosphere as a measure of the worldwide nuclear activity.

Equipment and Infrastructure Cost (US\$)

There are no published costs and each country now performing such measurements will likely have a different estimate depending upon other uses for which the equipment is used and when the installation was made. However, the lowest cost of the equipment which could be available is:

Field collector	-	3,000
Preparative gas chromatograph	-	3,000
Analytical chromatograph	-	2,000
Scintillation gas radiometer	-	5,000
Standard gases	-	2,000
Bottles for shipping samples (each)	-	100

Personnel Requirements and Training

The estimates below are subject to considerable uncertainty:

Personnel:	Field technician	- 2 hours per day for collection - 1 day per month for equipment maintenance
	Central Laboratory	- 1 hour per month supervision by radiochemist - 2 full-time technicians (for about 10 samples per month)
Training:	Field technician	- 1-week training
	Central Laboratory supervisor	- experienced professional radiochemist
	Central Laboratory technicians	- 3-month training

References

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5.3 Lead-210

Importance

Lead-210 (^{210}Pb), which has a radioactive half-life of 22.26 years, is produced in the lower troposphere from the decay of ^{222}Rn through a series of five progeny in the atmosphere. Atoms of ^{210}Pb attach themselves to submicron-size aerosol particles, and, therefore, act as aerosol-borne particles in the lower atmosphere since ^{222}Rn gas is mainly emitted from land surfaces. Because

of the attachment of ^{210}Pb to aerosol particles, ^{210}Pb is useful as a tracer for evaluating atmospheric deposition/removal processes. Measurements of ^{210}Pb combined with the well-known sources and sinks of ^{222}Rn gas serve as ideal tools to study the transport, mixing and deposition/removal processes that occur in the atmosphere. Lead-210 has been extensively used by scientists for validating their aerosol transport models and assessing the regional and global atmospheric circulations.

Siting Requirements

The mean residence time of ^{210}Pb is short compared with its radioactive half-life. Because of its short residence time in the atmosphere and its dependence on the distributions of atmospheric aerosols and the surface emanation rates of ^{222}Rn which varies with land surfaces, the interpretation of ^{210}Pb measurements is highly site-specific. Lead-210 has been routinely measured at both continental and remote global sites. Long range transport studies are also best made from coastal or high-altitude sites free of local ^{222}Rn sources.

Methods of Measurement and Sampling Frequency

The typical air sampling system for measuring ^{210}Pb includes an air sampler connected to an air pump with an electric motor. In the air sampler, an air filter exposed to the airstream collects all the ambient progeny. The typical range in the flow rates through an air filter is about 0.8-1.8 m^3/min . Frequent readings of the temperature and pressure drop across the filter are used for the calculation of the volume of air that is sampled. The filter is usually changed once a week. The weekly samples are composited to form monthly samples. The ^{210}Pb activity is determined by calculating the net activity in the 46.5 keV peak using a high-purity germanium (HPGe) detector.

Data Reduction

The activity of ^{210}Pb is determined by computer analysis of the spectral data from both monthly composite and weekly samples. The lower limit of detection (LLD) of ^{210}Pb varies with the sample activity, detector, and counting time. The monthly composite samples are compressed into a 45- cm^3 plastic planchet which is put on the top of detector for analysis. The weekly samples are compressed into a 1-2 cm^3 cylinder, that can be analyzed by using a detector with a 1.5 cm diameter well. The approximate LLD for ^{210}Pb using a 16 hour counting time, in the monthly composite and weekly samples are 500 mBq and 50 mBq, respectively. The minimum detectable concentration for monthly composite samples using an air sampler having a flow rate of about 1.2 m^3/min is about 19 Bq m^{-3} . The minimum detectable concentration for weekly samples using an air sampler having a flow rate of about 0.9 m^3/min is about 28 Bq m^{-3} .

Archiving Procedures

The information on the collected samples, dates, air volume and the analyzed concentrations of ^{210}Pb that are stored in the computer are linked to EML's web site.

Application of Results

The ^{210}Pb data can provide useful information for tracing chemical components in the atmosphere. For example, low ^{210}Pb concentrations with respect to high ^7Be concentrations can indicate subsidence of air from upper altitudes, which might explain a simultaneous increase in ozone concentrations. The data has also been extensively used by scientists to determine the mean residence time of atmospheric aerosols and to validate the wet scavenging processes in their aerosol transport models.

Equipment and Infrastructure Cost

No commercial ^{210}Pb measuring device is presently available. An air sampling device including an air sampler and an air pump may cost about US \$5,000 to construct.

Personnel Requirements and Training

Personnel: Field operator - 1 hr per week for changing air filter, handling and shipping the samples
Central Laboratory - 10 hrs per sample per month for data reduction, archive and dissemination

Training: Field operator - 1-week training
Central Laboratory technicians - 3-month training of professional radiochemist

References

Feichter, J., R.A. Brost and M. Heimann, Three-dimensional modeling of the concentration and deposition of ^{210}Pb aerosol, J. Geophys. Res., 96, 22447-22460, 1991.

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5.4 Beryllium-7

Importance

Beryllium-7 (^7Be), which has a radioactive half-life of 53.44 days, is produced by spallation reactions, disintegrations of nuclei of nitrogen and oxygen atoms that have been hit by cosmic-ray neutrons in the upper troposphere and the lower stratosphere. Because atoms of ^7Be quickly attach themselves to submicron-size aerosol particles in the upper atmosphere, the particles move downward from the upper atmosphere until wet scavenged. While the particles carrying ^{210}Pb travel upward from the lower atmosphere until wet scavenged, the use of ^7Be and ^{210}Pb together are considered to be an excellent combination for examining the wet scavenging parameterization in the atmospheric transport model. There are not only vast amounts of ^7Be data available, but also well-defined source distributions of ^7Be that can be used for model simulation. In addition, the concentration ratio, $^{10}\text{Be}/^7\text{Be}$, is an ideal indicator for evaluating the mass exchange between the stratosphere and troposphere in the upper atmosphere, since ^{10}Be has a much longer half-life of 2.7×10^6 years.

Siting Requirements

Beryllium-7 is produced naturally in the upper atmosphere by a cosmogenic source. About 67% of the ^7Be source is in the stratosphere and the rest is in the troposphere. The level of measured concentrations of ^7Be can depend on the site where it is located in the high mountain or

at low elevations. Likewise high concentrations of ^7Be are measured around the inter-tropical convergence zone where there is high convective precipitation.

Methods of Measurement and Sampling Frequency

The air sampling system described in Section 5.3 for collecting ^{210}Pb is also used for ^7Be . Because an air filter exposed to the airstream collects all the ambient radionuclides, the ^7Be is collected weekly and a monthly sample is composed from weekly samples. The ^7Be activity is determined by measuring the 477.59 keV gamma using a HPGe detector.

Data Reduction

The activity of ^7Be is determined by computer analysis of the spectral data from both monthly composite and weekly samples. The lower limit of detection of ^7Be also varies with the sample activity, detector, and counting time. As already mentioned for ^{210}Pb , the monthly composite samples are analyzed by a coaxial detector, while the weekly samples are analyzed by using a well detector. The approximate LLD for ^7Be using a 16 hour counting time, in the monthly composite and weekly samples are 300 mBq and 45 mBq, respectively. The minimum detectable concentration for monthly composite samples using an air sampler having a flow rate of about $1.2 \text{ m}^3/\text{min}$ is about 12 Bq m^{-3} . The minimum detectable concentration for weekly samples using an air sampler having a flow rate of about $0.9 \text{ m}^3/\text{min}$ is about 25 Bq m^{-3} .

Archiving Procedures

Information on the collected samples, dates, air volume and the analyzed concentrations of ^7Be that are stored in the computer are linked to EML's web site.

Application of Results

As mentioned before, the ^7Be data combined with the ^{210}Pb data could provide useful information for tracing chemical components, such as ozone in the atmosphere. The concentration ratio, $^{10}\text{Be}/^7\text{Be}$, is an ideal tool to indicate stratospheric air mass intrusions into the troposphere. The ^7Be data has also been widely used by scientists in their aerosol transport models to validate the wet scavenging processes that occur in the upper atmosphere.

Equipment and Infrastructure Cost

No commercial ^7Be measuring device is presently available. There is no need to build another device for ^7Be because the air sampling device for collecting ^{210}Pb , cost about US \$5,000, can also be used here for collecting ^7Be .

Personnel Requirements and Training

- | | | | |
|------------|--------------------------------|---|---|
| Personnel: | Field operator | - | 1 hr per week for changing air filter, handling and shipping the samples |
| | Central Laboratory | - | 10 hrs per sample per month for data reduction, archive and dissemination |
| Training: | Field operator | - | 1-week training |
| | Central Laboratory technicians | - | 3-month training of professional radiochemist |

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6. SOLAR RADIATION

6.1. Solar Radiation Measurements (Direct, Total, and Diffuse)

Importance

Solar radiation at the Earth's surface is the principal source of energy responsible for maintenance of the world's climate, as we now know it. Surface solar radiation also provides the possibility of using a very small amount of that energy for controlled heating and electrical power generation. Basic principles in atmospheric science suggest that changes in the amount of solar energy received at the surface will affect atmospheric thermodynamics and hydrodynamics, although the exact mechanisms by which a given change in solar radiation will affect any particular atmospheric variable are very complicated and poorly understood. Accurate and long-term measurements of solar radiation over a large and representative portion of the globe will aid in determining energy deposition and transport mechanisms responsible for the planet's climate and its variations. Such ground-based networks along with satellite radiation observations form a complimentary system. The surface measurements furnish ground truth, and the space observations provide global coverage and a measure of variability. Such measurements assist the efficient and intelligent use of solar power for technical applications to human domestic and industrial needs.

Siting Requirements

Surface solar radiation is highly variable in time and space. Siting requirements for solar power utilization may vary from those seeking regional representativeness for climate studies. For solar power utilization the best site will be that at which the power application is to be made or from a site or set of sites near enough that measurements are representative of conditions at the prime site. For climate applications, the site must be free of sub-grid scale influences. The global climate grid scale of interest will depend on the spatial resolution of the diagnostic and analytic tools used in a particular climate study. In general, a solar radiation measurement site will be useful in climate analysis, if free of local influences such as orographic cloud effects, localized moisture or pollution sources. The site must provide a stable platform from which to make the observations and have access for routine instrument inspection and maintenance. For exact siting criteria, the reader is referred to the CIMO Guide or the BSRN Operations Manual (see references).

Methods of Measurement and Sampling Frequency

Several commercially available sensors are used for surface solar radiation measurements. Proven reliability, accuracy, and precision can vary widely between types of sensors. Accuracy and precision for individual sensors should be established by experienced personnel prior to and during field use. The calibration of the sensors should be directly traceable to the world standard maintained by the World Radiation Centre (WRC) in Davos, Switzerland. Pyranometers should be used with good ventilators. Routine and frequent, approximately once per year, calibrations and/or comparisons of the field sensors are required to maintain maximum measurement accuracy. Information on the best type of instruments for use at a given location and procedures on calibration can be obtained from either WMO recognised National or Regional Radiation Centres. The instruments are generally passive and relatively simple electronically, although a data acquisition system is required to collect information output from the instruments. To obtain a complete radiation balance at the surface, measurements of both the downward and upward fluxes of both solar and terrestrial (infrared) radiation are necessary. The simplest means of measuring this net flux is by using a net pyrradiometer, but for climate change studies this is not recommended. A multiple instrument suite, including pyranometers for the measurement of global, diffuse and reflected irradiance, a pyrliometer for the measurement of direct irradiance, and pyrgeometers for the measurement of upward and downward directed terrestrial irradiance are required. The pyranometer measuring diffuse irradiance must be shaded, and for the highest quality downward terrestrial irradiance the pyrgeometer should also be shaded. The pyrliometer

requires a solar tracking device. Routine inspection of the instruments is necessary to ensure the orientation of the tracking or shade device, operation, cleanliness of optical surfaces and apertures, and time-stamp and operations of the data collection device. Ideally, the instrumentation should be checked and cleaned daily and following significant weather events (e.g. dust storm, snow) if the highest quality data is sought. Solar radiation affected by clouds can vary significantly on time scales of less than 1 second, but few sensors are capable of responding to such variations. Typically, the shortest time scales of solar radiation variability are ignored, but averages or sums compiled from 1-second samples are common. Averaging times vary from less than 1 minute to a few minutes to 1 hour. It is recommended that for quality assurance procedures, the frequency be as high as practically possible to a limit of 1-second sampling and approximately 1-minute averages. Hourly, daily, and monthly sums and averages are often used in climate analysis, whereas nearly instantaneous values are used in some engineering and scientific applications.

QA/QC

For the best data, daily quality assurance checks are essential. The most simple method of determining the general quality of the data is by plotting the data, at the highest frequency possible, against solar time. Using such simple plots a moderately trained technician is capable of determining problems associated with both the instrument and the data acquisition system. On clear days with higher frequency sampling, drifts in the clock can also be detected and corrected. More elaborate quality assurance schemes can be implemented as more measurements are made at the site. The BSRN World Radiation Monitoring Centre provides a number of quantitative checks in its data archiving manual (see references). For data stored on timeframes of an hour or longer, the World Radiation Data Centre can provide information on quality assurance. Since 1980, the World Radiation Centre in Davos, Switzerland, has been maintaining the World Radiometric Reference represented by a group of 7 absolute cavity radiometers. Regional standard radiometers are linked to that reference by international comparisons every 5 years; IPC-IX was held in 2000 at Davos.

Ancillary Measurements

The increasing need for multiple types of data to address environmental problems should encourage those deploying instrumentation to set up the radiation station at locations where meteorological and/or atmospheric chemistry measurements are already routinely obtained. At locations where this is not possible, the measurement of basic meteorological variables (e.g. temperature, pressure, humidity) should be considered the minimum ancillary observations. The measurement of aerosol optical depth (AOD) and ultraviolet (UV) radiation are also considered as complimentary measurements to solar and terrestrial radiation. For more scientific purposes, co-location with upper air sounding stations is useful, especially when UV and aerosol measurements are also made at the same location.

Archiving Procedures

Besides local and national archives, data is archived at the World Radiation Data Centre (WRDC), Main Geophysical Observatory, St. Petersburg, Russian Federation and the World Radiation Monitoring Centre (WRMC) ETH, Zurich, Switzerland. Detailed information on archival procedures can be obtained directly from each centre. The former one archives all forms of radiation data at timescales of one-hour or longer, while the latter is the archive for WCRP/BSRN data.

Application of Results

Data are applied to the scientific and engineering problems discussed in previous sections.

Equipment and Infrastructure Cost (US\$)

Direct Sun

Tracker - 2,000 (clock drive) to 10,000 + (computer drive)
Pyrheliometer - 2,200

Total Global

Pyranometer - 1,700

Diffuse

Pyranometer - 1,700
Shade band - 1,700 (semi-fixed)

Infrared (Terrestrial)

Pyrgeometer - 1,700 - 3,500

Net Radiation

Net Radiometer (Net pyrradiometer) - 1,500 - 4,500

Data System

Field-type data-logging (battery back-up), 10 Channel - 2,500
Laboratory style, integrating, multiple channel, microvolt resolution -
Misc. supplies, cables, connectors - 1,500

Calibration Facility

Absolute cavity - 10,000
Pyrheliometer - 2,200
Pyranometer - 2,200
Solar tracker - equatorial mount - 2,000
two axes - 20,000
Shade device - 1,700 (can use two-axes tracker and shading assembly)
Data system - 3,500
Travel to interact with calibration standards - 2,000 per year

Comparison of absolute cavity radiometer (Regional or International Pyrheliometer comparison - 8,000 once per 5 years)

Data Processing

Computer - 5,000
Peripherals - 3,000
Software - 2,100 + 500 per year
Misc. supplies - 500 per year

Personnel Requirements and Training

Personnel: Field site technician or scientist with interest in atmospheric processes - 20 minutes per day.
Calibration facility technician or scientist with solar radiation experience - 1 month per year plus 2 weeks per year for each field site (Note: field site could be calibration facility)

Training: Field site - 1-2 days plus exposure to different conditions
 Calibration Facility - 1 month
 Data management and quality evaluation – 1 month

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6.2 Ultraviolet radiation

Importance

Ultraviolet (UV) radiation reaching the Earth's surface is classified into two domains: UV-A (315-400 nm) and UV-B (280-315 nm). UV-A is only slightly affected by ozone, while the steep atmospheric cut-off in the UV-B range (around 290 nm) is caused by the absorption of UV radiation by ozone in the atmosphere. This range is of crucial importance for photo-biological processes inducing several biological damages on living cells and plays a major role in the deterioration of numerous non-biological materials. In addition UV radiation strongly affects photochemistry, e.g. by the production of OH radicals. In general, the shorter wavelengths in the UV-B region are increasingly more effective and, therefore, variations in ozone will have a strong effect on the surface irradiance [WHO, 1994; WMO, 1998].

With the ozone layer currently being in its most vulnerable state, monitoring UV along with other factors such as clouds, aerosols, albedo and pollutants is extremely important for defining the

UV field at regional and worldwide scales, as well as determining, quantitatively, the factors that affect the surface UV dose.

Methods of Measurement and Sampling Frequency

UV measurements of all types are continuing to expand and the number of sites undertaking UV monitoring is increasing, although there is a lack of activity in the tropical regions and most monitoring occurs in the developed countries. To support the global network of UV measurements on an international basis, WMO has established a Scientific Advisory Group (SAG) on UV radiation, to address several aspects of data collection and use and aims at providing guidelines for instrumentation, calibration procedures, quality assurance and quality control of the data (WMO, 1999a; GAW report in preparation).

The instrumentation used for UV monitoring at the Earth's surface comprises four basic classes of UV measuring devices: spectroradiometers, broadband radiometers, filter radiometers and biological dosimeters (WMO-UMAP, 1996; EC, 1997).

Spectroradiometry measures the total UV radiation in spectral intervals of narrow band pass. The advantage of this technique is its versatility, the data being for example used for identifying the causes for trends. Moreover, if the action spectrum of a chemical or biological process is known then a knowledge of the incident radiation spectrum can be used to calculate its potential effect (e.g. the dose for erythema and DNA damage in the UV waveband). Although the number of routine solar spectral monitoring sites is increasing, the number of instruments which can produce spectral UV measurements of sufficient quality and reliability are limited.

Broadband UV detectors for environmental monitoring have been more extensively deployed during the last decade. Broadband radiometers measure the total irradiance contained in a specified waveband (the weighting usually approximates that of erythema). The broadband measurement has advantages in temporal resolution and ease of use, nevertheless, that come at the cost of less information and versatility in the use of data and analysis: a broadband instrument provides no information about the spectrum of the incident radiation and if a change in the radiation source is detected it is not possible to determine whether the change is spectrally dependent or a uniform change at all wavelengths. Furthermore, these measurements must be accompanied by an appropriate QA/QC programme.

A further class of instrumentation, the multi-channel filter radiometer, has recently become available and provides information on several narrowly defined regions of the spectrum (e.g. short wavelength UV-B, the UV-A/UV-B border region, UV-A and Photosynthetically Active Radiation (PAR)). It has many of the practical advantages of the broadband instrument, but also provides some spectral information. Data analysis allows calculation of total ozone amount and the full UV spectrum. Most of the currently used instruments have been deployed in the 1990s and further analysis needs to be made to estimate the real capabilities of such instrumentation for trend detection.

Finally, dosimetry is a simple technique for measuring the dose of radiation received by a given surface over a specified period of time. It usually implies a small badge-like sensor made of a biological material. One widely employed UV dosimeter, which is also commercially available, is polysulphone film. The film changes its absorbance at 330 nm on exposure to UV radiation and has a response spectrum similar to the erythemal action spectrum. Another technique utilizes the DNA damage of bacteria due to UV radiation. Dosimeters are suited for situations where the use of radiometers is not possible (e.g. assess the actual exposure of mobile surfaces), but suffer from the same restrictions as broadband meters and can provide doses (temporal integrals) only. Most of them in use today are research tools and still under development.

Besides measurement activities, modelling of the radiative transfer of UV radiation has become an important and challenging part of the interpretation of the observations. Radiative transfer models have been applied in the development of satellite-based methodologies for

deriving the UV irradiance on the Earth's surface. UV monitoring from space offers the unique opportunity to achieve a global coverage of the UV radiation field and is a very promising tool once adequately validated. Recent efforts have allowed the estimation of the global distribution of solar UV radiation taking into account the impacts of ozone, cloudiness, aerosols, albedo and altitude [Herman et al, 1996], [Verdebout et.al. 2000].

QA/QC

To enable measurements from different types of UV instruments to be used in a network, the measurements must be related to a commonly acknowledged standard by careful calibration and operation. The calibration procedures, the instrument characterization and the conditions under which measurements are made must be clearly defined as they all contribute to the uncertainty associated with a measurement. It is vitally important that the uncertainty in a measurement is assessed so that false assumptions of uncertainty are not made in using the data. International UV instrument intercomparisons have served as an important element in improving quality assurance (QA) and quality control (QC) practices [Gardiner et al., 1993; Leszczynski et al., 1997]. The actual estimations of minimum uncertainty for the best UV instruments are of the order of 5% [Bernhard and Seckmeyer, 1999].

Ancillary measurements

UV data in isolation are of limited use, ancillary measurements are required. Additional information should be provided on background operational details: where, when and how were the measurements made, including instrument characteristics and uncertainty limits.

Where considering radiation measurements, a site description is necessary. Any feature of the site that could influence radiation measurements should be recorded (details of obstructions, rough approximation of the albedo, downwind of a heavy industrial area, etc.). Furthermore, application data is required for the interpretation of results in the context of their intended analysis (e.g. ozone measurements, information on cloud coverage, temperature, aerosols, albedo, quantitative information on air quality).

Archiving procedures

The World UV Radiation Data Centre (WUDC) resides in Toronto, Canada. It is established as a twin to the global ozone database (the World Ozone Data Centre) because of the evident relationship between UV and ozone (WMO, 1998). The last decade has seen a tremendous increase in the number of UV monitoring sites and, recently, in the efforts to enable the information gathered to be linked together and used as a single database. It is a challenge addressed by WMO to complement and establish the infrastructure for a central data management and quality assurance facility, which will enable data from a multiplicity of UV instruments to be harmonized and used as a global dataset by interested parties. Data are also archived for special research purposes in regional databases such as the European UV database (<http://www.muk.uni-hannover.de/EDUCE>).

Data analysis

Data analysis are often done on site with the instrument calibration parameters and ancillary measurements. Central management of radiation measurements made at all sites is mandatory if reliable measurements are to be realized.

Application of results

UV radiation affects many forms of life either directly (human health effects on the skin, the eye, immune system, effects on ecosystems) or indirectly through reactions, which influence the quality of life (air quality, materials, food supply). DNA belongs to the most critical target for damage by UV, since ultraviolet light can break the bonds of DNA molecules, which occasionally

are not repaired, leading to dangerous forms of skin cancer in humans (basal, squamous and melanoma). Monitoring surface UV radiation and quantifying future changes is therefore of great importance in support of environmental assessments and environmental information for the public, e.g. the application of national UV index programmes related to UV forecasting. [WMO, 1999b; ECUV 2000].

Equipment and infrastructure cost (USD)

Broadband UV sensor -	5,000 (one-time cost)
Spectroradiometer	100,000 (one-time cost)
Total startup cost	5,000 or 105,000
Various costs for maintenance and radiometric calibration apparatus	
Central processing and calibration facility -	65,000

Personnel requirements and training

Personnel	Central Radiation Facility – 1 full-time radiation expert and 1 half-time data processor assistant
Training	for low-resolution instrument – 1 month for high-resolution instrument – 1 year

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7. OTHER MEASUREMENTS

7.1 Volatile Organic Compounds

Importance

Volatile organic compounds (VOC) (a subgroup of non-methane hydrocarbons, NMHC) are recognized to be important precursors of tropospheric ozone, as well as other oxidants and organic aerosols.

The production of ozone and other photo-oxidants in the troposphere by reactions of volatile organic compounds (VOC), nitrogen oxides and sunlight is recognized as a serious global environmental problem. In order to design effective control measures for the reduction of photo-oxidants, photochemical processes have to be understood and the sources of the precursors known. Reliable and representative measurements of VOCs are necessary to describe the anthropogenic and biogenic sources, to follow the photochemical degradation of VOCs in the troposphere, and to assess the effectiveness of control measures. Measurement of VOCs is of key importance for the understanding of tropospheric chemistry. A portion of VOCs found in the atmosphere are the NMHCs containing only carbon and hydrogen this fraction constitutes the majority of anthropogenic VOC emissions. The analytical methods available for NMHC determination are up to now less demanding than for the other chemical classes constituting the VOCs.

Siting Requirements

Tropospheric VOCs (NMHC) have been one of the recommended measurements to be made at global sites under the GAW programme. The purpose will be to monitor their atmospheric abundance, to characterize the various compounds with regard to anthropogenic and biogenic sources and to evaluate their role in the tropospheric ozone formation process. Because of their relatively short residence in the troposphere, a representative background level can not be easily established, since it would require hundreds or even thousands of measurement sites. Therefore, the initial objective for VOC/NMHC monitoring focuses on the chemical characterization of the air masses in the vicinity of global stations.

Because of the very different residence time in the atmosphere for the individual compounds no background level can be readily determined, but the mixing ratios and compound ratios can be used for characterization of the photochemical age of air masses and transport processes. At global GAW sites anthropogenic and biogenic sources are present and the measurements reflect the regional tropospheric ambient air quality. Measurements are also needed as input for global/regional climate modeling based on CTMs.

Methods of Measurement and Sampling Frequency

An international WMO/GAW panel of experts for VOC measurements developed the rationale and objectives for this GAW activity and recommended the configuration and required activities of the World Calibration Centre (WCC) for VOCs (WMO Report No. 111, 1996). In reflection of the complexity of VOC measurements and the current status of measurement technology, a "staged" approach was adopted.

Stage 1 measurements: C2-C9 hydrocarbons, including alkanes, alkenes, alkynes, dienes and monocyclics.

Stage 2 measurements: C10-C14 hydrocarbons, including higher homologs of the Stage 1 set as well as biogenic hydrocarbon compounds.

Stage 3 measurements: Oxygenated VOCs, including alcohols, carbonyl compounds.

The panel of experts recommended the implementation of a VOC Demonstration Network consisting of a subset of GAW Global Stations where the VOC measurement programme for stage 1 will be performed via the collection of air samples with suitably prepared canisters.

Only chromatographic methods are suited for the atmospheric monitoring of VOCs, numerous different compounds have to be determined individually at trace levels. Most methods for the determination of NMHCs employ gas chromatography with flame ionization detection (FID); other detectors (MS, PID) have also been used. Two procedures are established for the monitoring of ambient air, namely grab air sampling into suitable canisters, with subsequent analysis in the laboratory, and real-time sampling with on-line analysis at the monitoring site. Both techniques require an enrichment step due to low NMHC concentrations in the ppbv to pptv range. Commonly, sample volumes of 100 to 1000 cm³ are concentrated in an adsorptive or cryogenic trap. The thermally released sample is usually refocused on the GC column to provide a sufficiently narrow injection band before the chromatographic run. For the subsequent separation, usually thick film WCOT columns with a nonpolar stationary phase (e.g., DB-1, DB-5) or the more strongly adsorptive PLOT columns (e.g., alumina (A1203) PLOT columns deactivated by KCl or Na₂SO₄, PoraPlot) are used. Sub-ambient oven temperatures (down to -50°C) are necessary even with thick film capillary columns to separate the C2 and C3 NMHCs. PLOT columns separate this fraction above room temperature but only C2-C8 NMHCs elute from these columns. This range may be extended to C9 by raising the GC oven temperature above the maximum column temperature for a short period of time.

The storage/shipment time of canister samples must be as short as possible. The filled canister samples have to be analyzed within one week after sampling and the filled canisters should not be exposed to extreme temperatures (heat and cold).

Ancillary Measurements

The most important ancillary measurements are meteorological data including wind speed and direction, temperature, dew point, pressure, spectrally resolved solar radiation ($J(O_D)$) and $J(NO_2)$ and oxides of nitrogen.

Archiving Procedures

Reactive Gases – VOC/NMHC are archived at the World Data Centre for Greenhouse Gases operated by the Japan Meteorological Agency, in Tokyo.

Data Analysis

The final analysis of the recorded GC spectrum yields identified VOC/NMHC compounds and their concentration levels.

The calibration, quantification and peak identification depend on the detector. When using PID and MS as a detector, individual calibration of each target compound is necessary. As this is impractical for more than 50 NMHC compounds in the range of C2 to C9, FID is the most frequently used GC detector for NMHC measurement. The quantification may then be made using the unique constant molar response factor of the FID or known carbon response factors, deviations were shown to be less than 15% for most of the NMHCs. FID response of ethyne is strongly dependent on the operation conditions of the FID. Ethyne thus can be quantified properly only when using an ethyne containing calibration gas mixture.

Application of Results

Data obtained by VOC/NMHC monitoring programmes are used to assess the ozone/organic aerosol formation potential and the attribution of VOC/NMHC to biogenic versus anthropogenic sources. The data are also an important input requirement for global/regional chemistry transport models (CTMs).

When fully operational, the sampling frequency at global GAW stations will be one per day, whereby the time of sampling must be determined by the station manager based on meteorological considerations.

As measurement technologies advance, an alternate approach is likely to be implemented allowing for the installation of continuously operating GC instruments at the global sites and thereby eliminating the need for canister samples.

QA/QC

Many activities are required to insure high-quality VOC/NMHC data. At the highest level, these activities include maintaining several internally-consistent multi-component standard gas mixtures.

Individual calibration of each compound is to be preferred over quantification by a single carbon response; carbon response factors give information about the analytical system e.g., for possible losses of C2 to C3 and >C8 NMHCs.

Regular scientific scrutiny of the data can occur only if a reasonable database management system and graphics capability to view data in near-real-time are available.

Experts should regularly examine data to insure the values and compound ratios are reasonable (e.g., I-Butane/Butane or Benzene/Toluene), and to begin searching for the reasons if they are not.

Quality control can also be enhanced by scrutinizing “engineering data” recorded from an analysis system such as pressures, temperatures, and flow rates. Additional QC information is available from chromatographic parameters that include peak retention time and peak width.

It is essential for measurement programmes to have redundancy built into them. When inconsistencies appear among duplicate measurements, then the search for the cause can start. Some examples of precautionary measures are:

1. Carefully collect discrete samples that can be compared with in situ measurements. Normally analyze at a central laboratory that also maintains a programme’s highest level standards.
2. Routinely analyze air from a “surveillance” cylinder as part of an in situ measurement programme (e.g., randomly once per day).
3. For in situ operations, use two different intake lines. If one intake has a leak inside the observatory building, it will be obvious when the results from the two lines are compared.
4. Analyze “test” samples from flasks that were filled from a cylinder of natural air. Test flasks should be analyzed every day that discrete samples are analyzed.
5. Share samples with other measurement programmes and routinely compare results.

There is no universal scheme to insure high-quality data; each programme should develop a scheme, with guidance from other successful programmes, suitable to their own needs.

Equipment Infrastructure and Cost (US\$)

A. Sampling

- Canister for sampling 1000 per canister
(typically 10 canisters per site are required to operate station at a daily sampling frequency, whereby the canisters are shipped to a central analytical facility for GC analysis)
- Canister shipping (max duration 7 days) t.b.d.

- Compressor for canister filling (1 per site) 3000

B. Analysis

- Central Analytical Facility – GC including data acquisition 40,000
- System for cleaning canisters 20,000
1 central facility can “serve” - in principal - up to 20 GAW stations
- VOC/NMHC standard gas mixture (gravimetric preparation) 6,000/year

C. Personnel Requirements & Training

- On-site sampling
-1 hour per day (operator needs on-site training for handling the canister probes)
- Central Lab
-1 full time staff (operator needs extensive prior training)

References

WMO-GAW Report No. 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)

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7.2. Persistent Organic Pollutants

Importance

Persistent Organic Pollutants (POPs) are, by definition, organic compounds that are chemically stable, liable to bioaccumulation, hazardous to human health and the environment and prone to long-range transport and deposition. Many POPs are relatively volatile and the atmosphere is one of the most important pathways for their transport and deposition to aquatic and terrestrial environments. The POPs are removed from the atmosphere through wet and dry deposition. Wet deposition includes scavenging of these compounds in both the gas and particle phases and dry deposition processes include removal of both particles and gases. Due to consecutive processes of deposition, evaporation (reemission) and atmospheric transport (multi-hop pathways) POPs may tend to be transported and deposited at higher latitudes.

In the environment, POPs usually occur as mixtures of congeners and the composition of these mixtures changes over time through partitioning (separation of different fractions in air, water, sediment and soil), chemical transformation and preferential bioaccumulation. Thus, for model validation, for assessment of deposition/reemission fluxes, as well as for studies of the fate and adverse effects of POPs, their measurements in other media than air (water, snow, vegetation and soil) and quantification of surface exchange processes have to be addressed in the future.

Taking into account the high cost and difficulty of POPs' analyses, a WMO/EMEP workshop held in 1999 recommended that as a first step the following POPs should be measured: polyaromatic hydrocarbons (PAH) including benzo(a)pyrene (BaP), polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB), chlordane and hexachlorocyclohexanes (HCH) including lindane (*gamma*-HCH).

Siting Requirements

Specific siting criteria for POPs monitoring have not yet been determined but they obviously should follow general criteria for GAW Regional Stations. It was recommended that for initial stage of POPs measurements in Europe, five sampling sites would be sufficient, being preferably located near the coast or at lakes taking into account the importance of the air/water exchange. The preferred locations are: Scandinavia/Baltic Sea, Northern Atlantic region, Continental Europe, Mediterranean region and South Atlantic region. Presently there are only a few POPs measuring stations in Europe mainly located around the North and Baltic Seas and in the Arctic.

Methods of Measurements and Sampling Frequency

For the start-up phase it was recommended to restrict the POPs measurements to high volume sampling of air (air flow rate of 20-25 m³/hour) with glass or quartz fibre filters and polyurethane foam. Partitioning of gas and particle phases between the adsorbent and the filter as well as chemical degradation during sampling should be taken into account. A sampling time of 24-48 hours once every week is presently recommended.

For deposition measurements, because of the variation in the sampling efficiency among different types of samplers, it is essential that all stations in a monitoring network use the same type of sampler. In the initial stage it is recommended that bulk samplers should be used at all stations. At least at two stations wet-only samplers should be used in parallel. The funnels of the samplers should be made of glass or should be Teflon-coated and the same type of adsorbent (polyurethane foam) should be used both for bulk and wet-only samplers. The deposition sampling period should be one month (or one week every month).

Analysis of POPs may be carried out using gas chromatography with an electron capture detector (GC/ECD), or with mass spectrometry (GC/MS) or by high performance liquid chromatography with a fluorescence detector (HPLC/FD), but recommendations on specific analysis methods for environmentally important POPs have not yet been made. Standard operating procedures (SOPs) and data quality objectives (DQOs) for these POPs need to be developed and the presently used sampling and analysis methods should be harmonized.

The cost for one analysis of POPs listed above was estimated to about US \$800.

Data Archiving

The POP data from sampling sites operated in Europe are presently reported to the EMEP Chemical Coordinating Centre (CCC) at the Norwegian Institute for Air Research (NILU), Kjeller, Norway.

References

- EMEP, 1998: EMEP Expert Meeting on Measurements of Persistent Organic Pollutants (POP) in Air and Precipitation, EMEP/CCC-Report 8/98.
- WMO, 1999: WMO/EMEP/UNEP Workshop on Modelling of Atmospheric Transport and Deposition of Persistent Organic Pollutants and Heavy Metals, volume I, GAW Report No. 136.

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7.3 Heavy metals

Importance

Heavy metals (HMs) are emitted to the atmosphere from both natural and anthropogenic sources. In most cases (main exception is Hg), emission of heavy metals occurs on particles. Following release into the atmosphere, heavy metals either deposit in the vicinity of the emission source or are subject to long-range transport via air masses. Their deposition from the atmosphere takes place either through dry deposition or by scavenging with rainwater. Due to their toxicity and bioaccumulation in various environmental compartments they can create adverse effects on the environment and human health. That necessitates the need to study and assess (by applying monitoring and modelling) emissions of man-made sources, pathways and levels of heavy metals in the atmosphere and in marine, freshwater and terrestrial environments. Available estimates show, for example, that from 50 to 96% of heavy metals (in soluble form), entering the World Ocean, deposit from the atmosphere. The most intensive studies of the atmospheric transport and deposition of heavy metals were conducted in North America, in Europe (EMEP) and for the North, Baltic and Mediterranean Seas.

The metals recommended to be included, for example, in an EMEP measurement programme are: 1. First priority - mercury (Hg), cadmium (Cd) and lead (Pb), 2. Second priority - copper (Cu), zinc (Zn), arsenic (As), chromium (Cr) and nickel (Ni).

Siting Requirements

The siting for HMs measurements should follow the same criteria as established, for example, for GAW regional or EMEP stations. In addition, further precautions have to be taken to prevent contamination from local sources (metal dust from pumps, metal surfaces, building materials, paint, etc.). For Europe (EMEP), about ten advanced stations ("super stations") with good geographical representation were recommended to start the measurements with an adequate coverage for verification of modelling results. They should be in northern and southern Scandinavia, western Russia/Belarus, southern Finland/Baltic, Baltic/Poland, central Europe/Czech Republic/Slovakia/Hungary, Balkan, Ireland/UK, Portugal/Spain, southern France/Italy, and Germany/Netherlands.

Methods of Measurements and Sampling Frequency

For measurements of HMs in precipitation the weekly sampling with wet-only or duplicate bulk samplers were recommended by two WMO/EMEP workshops held in 1996 and 1999. It is important that no parts of precipitation collectors are made of metal. Mercury is collected in special samplers made of polyethylene and glass.

High volume samplers capable of collecting two size fractions with separation at 2.5 and 10 μm are recommended for metals in airborne particles. Gold traps are recommended for gaseous mercury. For an initial stage, the sampling period and frequency is one 24 hours sample every week. For model validation, measurements of a daily resolution are necessary, but could be run in campaigns.

The Inductively Coupled Plasma Mass Spectrometry (ICP-MS) method was recommended as an analytical reference method for Pb, Cd, Cu, Zn, As, Cr, and Ni. The Graphite Furnace Atomic Absorption Spectrometry (GFAAS) and the Flame Atomic Absorption (FAAS) methods are also widely used. The GFAAS is more difficult and it is prone to interferences but its sensitivity is two-to-three orders of magnitude higher than FAAS.

The Cold Vapour Atomic Fluorescence Spectrometry (CVAFS) was recommended as an analytical reference method for Hg analysis. Accuracy and precision of HMs measurements in precipitation were established for GAW in 1992 (and may need revision). They are 1 ppb or 20% for the laboratory analysis and 30% for the overall operation. For measurements in air - they are 30%.

To improve the quality of HM analysis, laboratory intercomparisons are organized every year. Since 2000 that is done by the EMEP CCC.

Archiving Procedures

The GAW data on HM concentrations in precipitation are collected at the GAW World Data Centre for Precipitation Chemistry (Albany, USA). Data on chemical composition of aerosol are planned to be collected at the GAW Data Centre for Aerosols (Ispra, Italy). The EMEP data on HMs are collected by the EMEP Chemical Co-ordinating Centre, CCC (Kjeller, Norway).

References

- EMEP, 2000: Sampling of Heavy Metals, and Analytical Methods for Determination of Heavy Metals (drafts), EMEP/CCC -Notes.
- WMO, 1992: Report of the WMO Meeting of Experts on the Quality Assurance Plan for the Global Atmosphere Watch, GAW Report No. 80.
- WMO, 1997: Report and Proceedings of the Workshop on the Assessment of EMEP Activities concerning Heavy Metals and Persistent Organic Pollutants and their Further Development, GAW Report No. 117.
- WMO, 2000: Report of the WMO/EMEP/UNEP Workshop on Modelling of Atmospheric Transport and Deposition of Persistent Organic Pollutants and Heavy Metals, Volume I, GAW Report No. 136.

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7.4 Meteorological Parameters

Importance

An understanding of the climatology in the area immediately around and especially upwind of a GAW station is necessary for the interpretation of any long-term data that will be collected at the site. Any seasonalities, data extremes, and secular changes of meteorological parameters will need to be examined and put in context with the climate of the region.

Siting Requirements

The climatology, along with the topography and ecosystems of a site, must be described and understood in order to interpret the observations properly. It may be difficult to find a location that will meet all the requirements for measuring all species important to global change. Therefore, as a first step, the global change parameter(s) important for measurement and study within the region of interest should be identified, and then the best site in the region should be located where the most representative measurement of the parameter(s) can be made. If solar fluxes are important, then clear skies are a prerequisite; if CO₂ is important, then sources and sinks around and upwind of the site must be understood and quantified, etc. The climatology of the region must be of sufficient spatial and temporal homogeneity to ensure the broadest extrapolation of the results in both space and time. The influence of local factors such as local wind regimes, orographic rain bands/shadows, dust storms, or seasonal (such as slash and burn) fires must be identified and factored out of the long-term measurements if a broad extrapolation of the data is intended. The same procedure is applicable for infrequent local pollution sources, which must be identified and edited out of the data record. Similarly, sources and sinks of interest, such as swamps for methane or deserts for aerosols, must be situated upwind of the proposed site in such a way that the meteorological parameters will provide the best opportunity to measure its downwind effects after they have been mixed and must be representative of concentrations of the regional air mass.

Methods of Measurement and Sampling Frequency

Temperature wind speed and direction, pressure, relative humidity/dew point and amount of precipitation are the standard meteorological parameters that should be recorded at GAW stations. Meteorological instrumentation has been standardized around the world. A continuous and *in-situ* measurement programme of meteorological parameters will be necessary to complement and interpret the individual global change parameters as well as their chemical and dynamical transformations at each regional station. The measurements should be of sufficient frequency and accuracy to register the smallest variations in, and possible long-term increases of, the trace species investigated, to document changes in the Earth-atmosphere system. Automated meteorological stations are highly desirable for these applications.

In addition, all past climatological data of the site and region should be analysed and used to aid future analyses of the global change parameters measured at the station. Climatic classifications, ground cover, synoptic flow patterns, and evapotranspiration rates are some examples of complementary data sets that can be used to characterize the site and to interpret measurements.

One-time studies should be made when necessary to characterize the meteorological conditions at the site that can influence the measurements at the station. Local wind studies, seasonal boundary layer mixing depth studies, or a study of the frequency of seasonal storm tracts in the vicinity of the station are examples of such studies. Every aspect of the Earth-atmosphere should be studied and understood as much as possible in the region where GAW Regional Stations are set up.

Archiving Procedures

All meteorological data and data from special studies should become part of the stations data archive. GAW stations are also required to submit meteorological parameters to the appropriate GAW World Data Centres.

Equipment and Infrastructure Costs

Standard meteorological parameters of pressure, temperature, relative humidity, wind speed, wind direction and solar radiation are necessary for the interpretation of many of the background measurements made at GAW stations. A complete automated station including a data logger that records these parameters is available from commercial manufacturers and usually costs less than US \$10,000. If local expertise is not available for these measurements, WMO should be contacted to identify appropriate instrumentation and provide guidelines on data recording practices suitable for a GAW station.

References

WMO Guide to Meteorological Measurements, 1996, No.8, Sixth Edition. (Available from WMO.)

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ANNEX A

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ANNEX B

WEB SITES

WMO home page:

<http://www.wmo.ch/index-en.html>

GAW home page:

http://www.wmo.ch/web/arep/gaw_home.html

World Data Centres:

WOUDC (MSC, former AES)

<http://www.msc-smc.ec.gc.ca/woudc/>

WDCGG (JMA)

<http://gaw.kishou.go.jp/wdcgg.html>

WDCSO3 (NILU)

<http://www.nilu.no/projects/nadir/wdcso3/wdcso3.html>

WRDC (Voeikov Observatory)

<http://wrdc.mgo.rssi.ru>

WDCA (JRC)

<http://www.ei.jrc.it/wdca/>

WDCPC (SUNY)

<http://marble.asrc.cestm.albany.edu/qasac/data.html>

All data centres can be accessed through:

<http://marble.asrc.cestm.albany.edu/qasac/gawlinks.html>

EMEP:

<http://www.emep.int/>

