

GAW Report No. 209

Guidelines for Continuous Measurements of
Ozone in the Troposphere

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**GLOBAL
ATMOSPHERE
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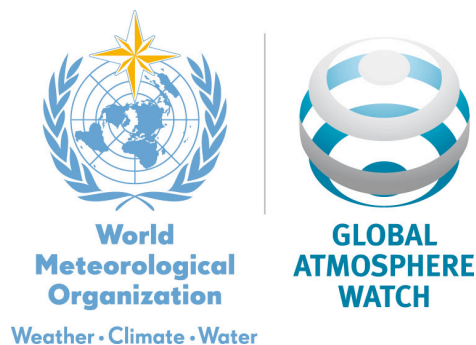
WORLD METEOROLOGICAL ORGANIZATION GLOBAL ATMOSPHERE WATCH

GUIDELINES FOR CONTINUOUS MEASUREMENTS OF OZONE IN THE TROPOSPHERE

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1. INTRODUCTION

Ozone (chemical formula O₃) in the troposphere (i.e. the lowermost part of the atmosphere, from the surface to 6-15 km height depending on the latitude) is highly relevant for the Earth's climate, ecosystems, and human health. Tropospheric ozone is the third largest contributor to greenhouse radiative forcing after carbon dioxide and methane (*Forster et al., 2007*). It is part of the Earth's shield against ultraviolet radiation, particularly when there is stratospheric ozone depletion (*Sabziparvar et al., 1998*). Ozone plays a crucial role in tropospheric chemistry as the main precursor for the OH radical which determines the oxidation capacity of the troposphere (*Seinfeld and Pandis, 2006*), it is a toxic air pollutant affecting human health (*Bell et al., 2006*) and agriculture (*Royal Society 2008*), and, through plant damage, it impedes the uptake of carbon into the biosphere (*Sitch et al., 2007*). Accurate long-term measurements of ozone in the troposphere, including near the earth surface in unpolluted and polluted environments, are needed in order to assess the impacts of tropospheric ozone on the earth system, human health and ecosystems, and to detect changes in the atmospheric composition which could aggravate or reduce these impacts because of changing ozone precursor emissions or climate change.

Quantitative measurements of surface ozone were first made over one hundred and fifty years ago (*Volz and Kley, 1988*). However, it was not until about the middle 1970s that surface ozone measurements acquired the higher reproducibility necessary for global background observations of ozone to detect spatial distributions and temporal variability (trends). The Global Atmosphere Watch (GAW) Programme of the World Meteorological Organization (WMO) aims to provide reliable long-term observations of the chemical composition and physical properties of the atmosphere which are relevant for understanding of atmospheric chemistry and climate change. Quantifying and understanding changes in tropospheric and near-surface ozone, and the environmental consequences of such changes, are a priority task identified by the reactive gases group within GAW. Reactive gases are one of the foci of the GAW Programme. This group includes ozone and its precursor species (carbon monoxide, volatile organic compounds and nitrogen oxides), and other short-lived gases which are inherently connected through various photochemical cycles in the atmosphere.

Atmospheric observations coordinated by the GAW Programme complement local and regional scale air quality monitoring efforts. GAW aims at observations which are regionally representative and are normally free of the influence of significant local pollution sources. The tropospheric ozone data are stored in the WMO/GAW World Data Centre for Greenhouse Gases (WDCGG). By April 2012 the WDCGG contained surface ozone data from 98 stations worldwide, of which 45 stations have contributed data until at least the year 2010 (Figure 1). Global networks that include agreement on standardizations, and compatibility of data from different observational platforms and sites are of crucial importance for the early detection of regional and global changes in the composition of the atmosphere, especially in connection with changing anthropogenic emissions. Time series extending over decades are required to assess these changes with a given degree of confidence.

From consideration of the "WMO Global Atmosphere Watch (GAW) Strategic Plan: 2008-2015" (*WMO, 2007b*) and its Addendum (*WMO, 2011b*), the major objectives for the GAW global tropospheric ozone measurement network can be summarized as follows:

- To ensure that tropospheric ozone measurements made by different laboratories are compatible and meet common data quality objectives suitable for the detection of regional and global changes
- To determine the spatial and temporal distributions of tropospheric/surface ozone with sufficient spatial coverage suitable for the detection of regional and global changes
- To validate global chemistry climate models and associated ozone precursor emission inventories through comparisons between simulated and observed ozone concentrations
- To improve air quality forecasts by providing ozone observations reflecting the chemical composition in the rural and remote planetary boundary layer and the free troposphere in near real-time to data assimilation systems.

Ground-based in-situ continuous observations contribute only one aspect of a complete monitoring system for tropospheric ozone. The integration of GAW surface ozone measurements with data from ozonesondes, aircraft, ships and satellites is required in order to obtain a comprehensive understanding of the tropospheric ozone distribution and how it changes with time.

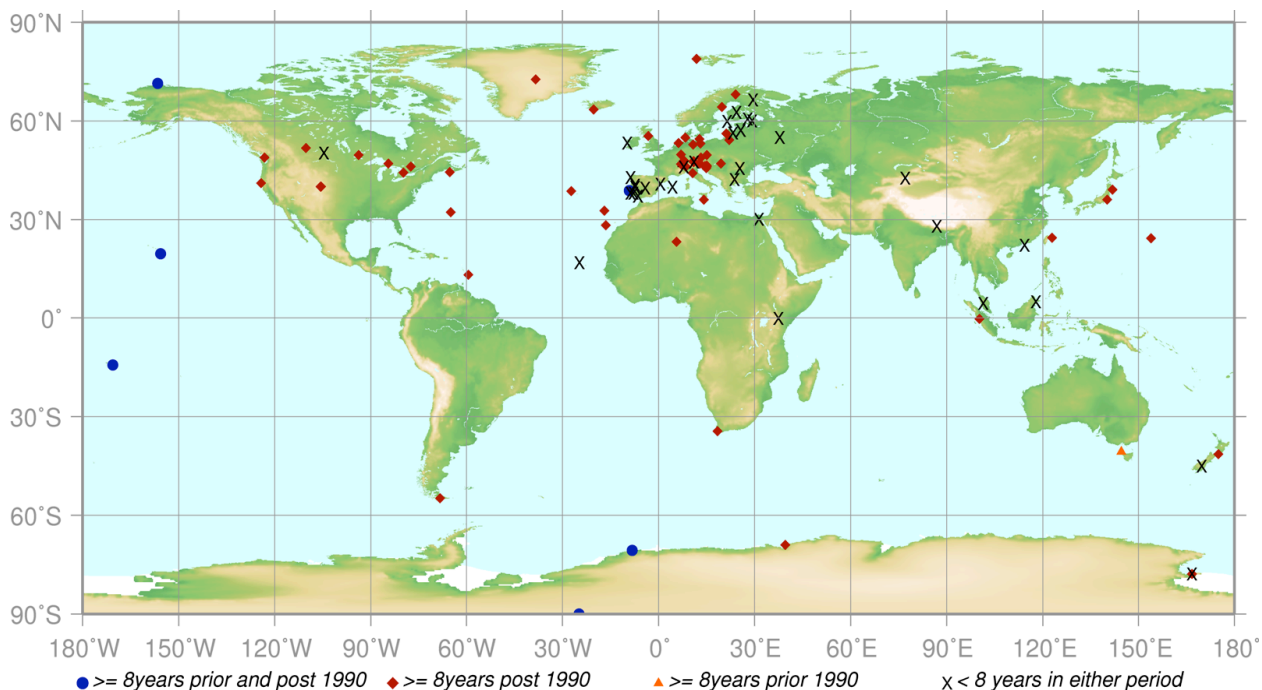


Figure 1 - Surface ozone sites and data coverage in the World Data Centre for Greenhouse Gases, Japan, 2012. Note that large portions of the Earth surface are severely under-sampled

The criteria necessary for integration are:

- The measurements from the different systems are compatible
- Each system has an evaluated combined measurement uncertainty
- That the uncertainties of measurement with each system are taken into account in combining the data.

Recent studies have attempted to consolidate the information on tropospheric ozone concentrations and their changes that can be derived from the different measurement platforms (*Chevalier et al., 2007, Brodin et al., 2011, Logan et al., 2012, Tilmes et al., 2012*). These papers evaluate the consistency between ground-based station data, ozonesonde measurements and measurements from the MOZAIC aircraft, and provide valuable insights into understanding the interaction of ozone in the lower atmosphere with that in the free troposphere.

It should be noted that there is also a need for better integration and harmonization of surface measurements between GAW and the various regional networks which have been implemented to monitor air quality. While GAW places its focus on measurements at remote sites, the distinction between remote and rural locations is not always clear. Numerical models are approaching grid scales where small-scale variations in ozone and its precursors can be simulated, and this creates a growing need for data sets that provide complete regional coverage and rely as much as possible on common calibration scales and quality control procedures.

Such globally harmonized observations and models can then be used:

- To better characterize and understand the processes that control tropospheric ozone and its budget

- To better understand tropospheric ozone trends, and to reconcile these with trends derived from the model simulations utilizing ozone precursor emission inventory data
- To contribute to the assessments of greenhouse climate forcing, ozone and surface UV radiation, the oxidative capacity of the troposphere and the role of ozone in health and food production.

More recently, ozone observations have been fed into modelling activities to enable data assimilation in forecasting systems and evaluate reanalyses of past atmospheric composition. Ultimately this model-data fusion should lead to improved assessments of the role of tropospheric ozone and other atmospheric constituents in environmental issues. A dedicated expert team within GAW seeks to enhance the near-real-time (NRT) transmission of GAW observations into the WMO information system (WIS) in order to facilitate the use of GAW data for these purposes.

The quality assurance (QA) system developed within the GAW Programme provides a unique framework to achieve the required measurement compatibility and harmonization¹. This QA framework is presented in the “WMO Global Atmosphere Watch (GAW) Strategic Plan: 2008-2015” (WMO, 2007b). The primary objectives of the GAW QA system are to ensure that measurement data are consistent, of known and adequate quality, supported by comprehensive metadata and sufficiently complete to describe global atmospheric states with respect to spatial and temporal distribution.

The detection and quantification of tropospheric ozone changes requires in particular that the long-term stability of the reference scale and its propagation to in-situ measurements are ensured. Furthermore, it demands careful documentation of the sampling and location characteristics including any changes in the surroundings of the measurement site which could, for example, add or eliminate local ozone precursor emission influences.

In this document we provide detailed guidance on the best practices in use for tropospheric ozone measurements. The focus is on continuous in-situ measurements of ozone in the troposphere, performed in particular at continental or island sites with altitudes ranging from sea level to mountain tops. The purpose of the report is to contribute to a convergence of these practices world-wide in the interest of promoting the principles and objectives of the GAW Programme, in particular to establish a harmonized global data set of tropospheric ozone observations. While the report’s primary focus is the consolidation of ozone measurement practices within the GAW Programme, we believe that many aspects covered in the following sections are also relevant for observations from other platforms (e.g., aircraft), and that they may be useful for improving regional air quality networks, particularly in countries with little experience or limited resources. Thus, these Measurement Guidelines for tropospheric ozone are intended for use at stations and any other measurement platforms, where such measurements have recently been added to the programme or will be added in the foreseeable future, as well as by institutions with experienced personnel and where work on tropospheric ozone has been performed for many years. This WMO/GAW Report was created under the auspices of the Scientific Advisory Group for Reactive Gases (SAG RG). This document replaces the Quality Assurance Project Plan (QAPjP) for Continuous Ground Based Ozone Measurements, GAW Report No. 97 (WMO TD No. 634), (WMO, 1994) as the Measurement Guidelines for tropospheric ozone, and is built upon that report.

¹The WMO/GAW Glossary of QA/QC-Related Terminology is available at <http://gaw.empa.ch/glossary/glossary.html#3.1>

2. HOW TO USE THESE GUIDELINES

These measurement guidelines describe the background, best practices, and practical arrangements adopted by the GAW Programme in order to enable the GAW station network to approach or achieve the defined tropospheric ozone data quality objectives.

These guidelines include information on: selection of station and measurement location, staff skills and equipment required, conduct of measurements, method for ensuring the quality and comparability of these measurements, data processing and data archiving. These cover the practical steps to be undertaken at each station to achieve the best possible ozone measurement.

As some readers may want to consider only part of the information provided, the following gives a breakdown of the guidelines.

Section 3: Defines tropospheric ozone data quality objectives with respect to the primary science objectives within GAW and according to other data needs.

Section 4: Establishes a stringent, quality-controlled and traceable calibration chain from a primary standard held at the Central Calibration Laboratory (CCL) to the transfer standards available at the World Calibration Centre (WCC).

Section 5: Provides recommendations for the choice of the measurement technique.

Section 6: Informs station operators about the measurement principles and limitations of the UV absorption measurement technique and provides recommendations how to detect and avoid potential measurement errors.

Section 7: Provides guidance on the set-up of a GAW station and in particular the ozone instrument.

Section 8: Establishes detailed operating procedures for ozone measurements.

Section 9: Establishes detailed procedures for the quality assurance of ozone measurements including the necessary actions to obtain a quality-controlled and traceable calibration chain from the World Calibration Centre to the ozone analyzer at the station.

Section 10: Provides guidance and support for data processing and data submission to the GAW data archive that stores the tropospheric ozone data (WDCGG).

Annex A: Provides background information about tropospheric ozone.

Annex B: Provides information related to the selection of new GAW surface ozone monitoring sites.

Annex C: Describes different instrumental methods for measuring tropospheric ozone.

Annex D: Describes different measurement platforms for tropospheric ozone.

3. DATA QUALITY OBJECTIVES FOR TROPOSPHERIC OZONE MEASUREMENTS

Data quality objectives (DQOs) define qualitatively and quantitatively the type, quality, and quantity of primary data required and derived parameters to yield information that can be used to support decisions. Data quality objectives (DQOs) were introduced to GAW in the 2000-2007 strategic plan (*WMO, 2001a*). At that time the detailed definition was: DQOs specify tolerable levels of uncertainty in the data, as well as required completeness, comparability and representativeness based on the decisions to be made. Since then the terminology of metrology has been clarified (*Joint Committee for Guides in Metrology, 2012*) and it is appropriate that the term compatibility is included in the DQO definition and practice, as is done here.

3.1 Units, quantities and measurands

The measurand, defined as the “quantity intended to be measured” (*Joint Committee for Guides in Metrology, 2012*) to be reported for tropospheric ozone measurements is the mole fraction of ozone in air expressed in the SI units of nmol mol^{-1} . During the last half century it has been common practice to report the volume mixing ratio expressed in parts per billion (ppb or ppbv). A recent review (*Davis, 2012*) of available data on the compressibility factors of air and ozone leads to the conclusion that for dry air at typical laboratory conditions the mole fraction of ozone expressed in nmol mol^{-1} is only 0.04% smaller than the corresponding volume mixing ratio expressed in ppbv. This requirement is satisfactory for the conditions of laboratory calibration. However it is necessary to know the compressibility factors for the full range of operating conditions for tropospheric ozone analysers. Because of the environmental conditions inside a GAW station, and the analysers’ own internal heating, commercial ozone analysers at GAW stations operate within the range 10 – 50 °C, 110 kPa to 50 kPa with air from fully dry to fully saturated. An examination of the literature (*Picard et al., 2008; Aparicio et al., 2009*), taking into account the arguments of *Davis (2012)*, indicates that the greatest deviation from the ideal gas law equation under GAW conditions would be a compressibility of $Z = 0.9995$, or a difference of 0.05%. This difference is smaller than the minimum detectable limit of any current instrument for measuring tropospheric ozone. For all practical purposes the two quantities can be used interchangeably and without distinction. Mole fraction is preferable, however, because it does not require an implicit assumption of ideality of the gases and, more importantly, because it is applicable also to condensed-phase species. For this report past and current studies that are reported in ppb retain those units. For future requirements and uncertainty analyses pertaining to future requirements the quantity is mole fraction with unit nmol mol^{-1} .

The mole fraction most appropriate to the chemical and physical interpretation of ozone measurements is the mole fraction of ozone in dry air. However, ozone measurements are usually made without sample drying, because an efficient system for drying air and leaving the ozone content of the air unchanged has not been developed. The International Union of Pure and Applied Chemistry, IUPAC (*Schwartz and Warneck, 1995*) acknowledged that atmospheric composition mole fraction values can be reported with respect to dry air and can also be reported with respect to moist air, if ‘there would otherwise be loss in accuracy or precision due to the conversion (to dry mole fraction)’. It is probably true that most lower tropospheric O_3 data, and probably most tropospheric O_3 data at WDCGG refer to moist air mole fractions, in contrast to other gases. The differences can be significant (up to 4.3% at 303 K and 100% relative humidity).

It is recommended that ozone measurements be accompanied by measurements of water vapour mole fraction of sufficient precision that the ozone measurements could be converted to mole fractions with respect to dry air without loss of precision. It is recommended that ozone measurements (where they were with regard to moist air) continue to be reported as mole fractions with respect to moist air and be accompanied by reporting of water vapour measurements. The key requirement is to have a clear statement of whether the ozone values refer to either dry or moist air mole fractions in the accompanying metadata.

This is discussed further in Section 6.3.

3.2 DQOs for key GAW goals

Tropospheric ozone measurements in the GAW Programme have the objectives to (a) detect long-term changes in ozone background concentrations and (b) quantify year-to-year variability in monthly mean background concentrations. (For a discussion on the characteristics of a background environment, see Annex B.) The justification of each of these objectives and the associated DQOs will be discussed in turn. This section quantifies what are tolerable levels of uncertainty in the data.

Two factors contribute to the detectability of a trend in tropospheric ozone, the instrumental measurement uncertainty and the seasonal, inter-annual and longer-term variability of the atmospheric mole fractions. *Weatherhead et al. (1998)* discuss the statistics of tropospheric ozone time series relevant to tropospheric ozone trends on time scales of a decade or longer. Where atmospheric variability is large, long-term measurements with small measurement uncertainty may still fail to detect an underlying trend because of the variability within the atmosphere. The DQOs are concerned primarily with instrument measurement uncertainty; the ability to detect a trend when the limiting factor is the measurement uncertainty.

Addressing the first objective, the observed tropospheric ozone trends suggest an approximate doubling of tropospheric ozone in the last 100 years. Consistent with this is a typical trend in tropospheric ozone of about 10% per decade, or, at an average mole fraction of 30 nmol mol⁻¹, a trend of 3 nmol mol⁻¹ decade⁻¹. (This is the same as the scientific objective defined by the previous ozone quality assurance measurement plan (*WMO, 1994*) of “must detect a change of 1% per year”.) To detect this tropospheric ozone trend, the combined measurement uncertainty must be approximately ± 1 nmol mol⁻¹ (two sigma) or less.

Zellweger et al. (2011) have introduced the discussion of measurement uncertainty associated with tropospheric ozone trends on time scales of a decade or longer. Each audit conducted by the World Calibration Centre for surface ozone hosted at Empa (for short here “WCC-Empa”) has an uncertainty associated with it. The maximum contribution that instrumental uncertainty can make to a trend in the ozone observations (provided the stations pass the audits) is the largest difference of the likely random excursions of the instrument calibrations from one audit to the next. To quantify this uncertainty a simplified analysis is made where audits are assumed to occur only at the beginning and end of a ten-year period. (The current statistics are that WCC-Empa conducts audits at stations typically every 4 years although intervals between audits of 8 years or more do occur.) Based on the normal distribution, there is a probability of 3% that the instrument calibration from the audits differs by one sigma in opposite directions from the first to the second audit. If the instrument has a combined measurement uncertainty of ± 0.5 nmol mol⁻¹ (one sigma) or ± 1.0 nmol mol⁻¹ (two sigma), then the result of the above mentioned drift would meet the DQO of ± 1 nmol mol⁻¹. Thus ± 0.5 nmol mol⁻¹ (one sigma) or ± 1.0 nmol mol⁻¹ (two sigma) is an acceptable level of combined measurement uncertainty in the context of tropospheric ozone trends. More frequent audits reduce the possible uncertainty in station observations.

The second objective of the DQOs is that the data should be sufficiently free of instrument noise so that the causes of year-to-year variability in monthly mean concentrations can be investigated, as these provide information about large scale atmospheric phenomena controlling tropospheric ozone. At remote sites such as Cape Grim, the year-to-year variability in monthly mean ozone mole fractions is ± 1 nmol mol⁻¹ (one sigma), which for the purpose of this analysis is regarded as all atmospheric induced variance. Then if the goal is that the instrument instability contributes less than 20% to the variance of the data, the DQO for year-to-year and long-term stability, as derived by the sum of the variances, is approximately ± 0.4 nmol mol⁻¹ (one sigma) or ± 0.8 nmol mol⁻¹ (two sigma).

Given the above, from the scientific perspective for decadal long stability of surface and tropospheric ozone measurements, a DQO of combined measurement uncertainty of ± 0.5 nmol mol⁻¹ (one sigma) or ± 1.0 nmol mol⁻¹ (two sigma) is recommended.

In practice, very few, if any, stations are able to meet these DQOs (*Buchmann et al., 2009; Klausen et al., 2003*), because of limitations arising from the uncertainties in current measurement systems. In the Sections 4, 8, and 9, these factors are discussed in more detail and recommendations are made about how these uncertainties can be evaluated and potentially reduced.

3.3 DQOs for model assimilation and validation

Recent initiatives to model and forecast atmospheric composition in near-real-time, NRT, (e.g. the European MACC project (<http://www.gmes-atmosphere.eu/>)) have expressed a strong interest in rapid data delivery for model evaluation. To serve this purpose an hourly concentration is required from the GAW station that shall be compared with the hourly concentration in the grid cell that encompasses the location of that station. The primary purpose of this comparison is to detect sudden changes in the data assimilation and modelling system (for example due to failure of a satellite sensor the data of which are being assimilated) and to identify potential extreme events (e.g. extraordinary biomass burning) which may need to be analyzed in more detail.

Considering this comparison, in the model grid cell, the mole fraction estimated by the model is both a time average (over a model time step, i.e. typically 10 minutes) and a “representative concentration” over the volume defined by the latitude range, the longitude range and the depth of the model grid cell. A mole fraction observed at the monitoring station represents a single point in space (within the grid cell) and the specified hourly average. There is a difference in what these two mole fractions represent. The issue is of up-scaling the concentration from a point measurement to a model cell of 10-100 km horizontal scale and 10- 200 m vertical scale. Specific scientific criteria and tools have been developed to understand the relationships between the modelled and observed mole fractions. Analyses of the spatial and temporal variability of ozone in the background atmosphere are required to improve this understanding.

Currently NRT applications require a combined uncertainty of less than $\pm 5 \text{ nmol mol}^{-1}$ (one sigma) for hourly values of unvalidated data and routine submission of preliminary data within 72 hours after sampling.

3.4 Completeness, comparability, compatibility and representativeness

Completeness is defined as the number of validated values for an aggregation period (period for which the data are collected) divided by the maximum possible number of valid values for the same period. This is also known as “data coverage”. Completeness can have a value from “0” to “1”. During an aggregation period, the number of values (data points) spent on quality control measurements (Span, Zero, Calibration), as defined in this Guideline, are not included in either the number of valid observations or the maximum possible number of valid observations for the purpose of estimating completeness.

The goal for completeness is 90% (*WMO, 1994; WMO, 2007b*). The minimum requirement for valid aggregation of the data is that the completeness should exceed 66% for continuous measurements and be uniformly distributed in time (*WMO, 2010b; WMO, 2011a*). When data are selected for particular conditions, different criteria for completeness will apply.

The WDCGG requires that the minimum coverage should be specified for converting minutely data to hourly averages, hourly data to daily averages and daily data to monthly averages (*WMO, 2009b*). In all cases, the data coverage of an aggregated value must be specified.

Comparability of measurement results is defined, for quantities of a given kind, as those that are metrologically traceable to the same reference (*Joint Committee for Guides in Metrology, 2012*). Comparability is achieved in GAW through the traceability of all measurements to the primary standard as discussed in the following sections.

Compatibility is defined as a “property of a set of measurement results for a specified measurand, such that the absolute value of the difference of any pair of measured quantity values from two different measurement results is smaller than some chosen multiple of the standard

measurement uncertainty of that difference” (*Joint Committee for Guides in Metrology, 2012*). The quantification of this requirement is provided in Section 3.2.

Representativeness of GAW observations is defined as “what spatial and temporal scales do the data represent” (*WMO, 2009a*). Representativeness of GAW observations should primarily be achieved through proper selection of the measurement site and the provision of an air sample inlet that avoids, in particular, influences of local sources and sinks on the measured species. This is discussed in the following sections.

The GAW tropospheric ozone measurement system currently has no redundancy checks built into it. More efforts should be put into the both use of a travelling instrument and joint instrument comparison campaigns for reactive gases including ozone to more fully quantify the compatibility and uncertainties of the measurements of tropospheric ozone mole fractions.

3.5 Recommendations for metadata inclusion

In order to make the tropospheric ozone data more useful in supporting decisions (*WMO, 2007b; WMO, 2011b*), a further recommendation is made to record the following metadata with the observations:

- The ozone absorption coefficient used to determine the ozone mole fractions (see Section 4.2.2)
- Whether the mole fractions are with respect to dry air or moist air (see Section 6.3)
- An agreed, standard set of data flags (see Section 10.3).

4. PRIMARY OZONE REFERENCE AND THE WORLD CALIBRATION CENTRE FOR SURFACE OZONE

4.1 Introduction

Compatibility in space and time of surface ozone data from different stations of the GAW network is of crucial importance for the early detection of global trends or slight variations in chemical composition of the atmosphere. In many cases, decades are required to assess these changes with a certain degree of confidence (*Weatherhead et al., 1998*). Thus, long-term stability of the reference scales is a prerequisite to meet the demanding objectives of GAW.

Within the GAW Programme, a dedicated quality assurance system consisting of the measurement stations and five different types of Central Facilities for each measured variable ensures comparable data (*WMO, 2007b; WMO, 2011b*). “The *principles* of the GAW QA system (*WMO, 2007b*) apply to each measured variable and encompass:

- Network-wide use of only one reference standard or scale (primary standard). In consequence, there is only one institution that is responsible for this standard.
- Full traceability to the primary standard of all measurements made by Global, Regional and Contributing GAW stations.”

The GAW Station shall ensure that “The GAW observation made is of known quality and linked to the GAW Primary Standard.” Adapted to the needs of tropospheric/surface ozone measurements, the responsibilities of the Central Facilities are (*WMO, 2007b*):

- The Central Calibration Laboratory (CCL) shall:
 - “Host in the long term (many decades) the GAW primary standard and scale for a particular variable.”
 - “Prepare or commission laboratory standards required by the GAW network members for calibration purposes.”
- The World Calibration Centre (WCC) shall:
 - “Assist Members operating GAW stations to link their observations to the GAW primary standard.”
 - “Develop quality control procedures following the recommendations by the SAGs, support the QA of specific measurements and ensure the traceability of these measurements to the corresponding primary standard.”
 - “Maintain laboratory and transfer standards that are traceable to the primary standard.”
 - “Perform regular calibrations and performance audits at GAW sites using transfer standards in co-operation with the established RCC²s.”³

Scientific Advisory Groups (SAGs) shall “Develop and approve methods to trace observations to the WMO primary standard.”

SAGs shall also: “Cooperate with metrology institutes both at international and national levels regarding the maintenance of measurement standards to ensure traceability to the International System of Units (SI) of observational data acquired in and provided from the GAW network” (*WMO 2011b*):

The purpose of the following sub-sections is to explain the physical basis of the primary ozone standard, its maintenance by the Central Calibration Laboratory (CCL) and a stringent,

² RCC, Regional Calibration Centre

³ Note that good practice in metrology stipulates that ideally audits and calibrations should not be performed by the same laboratory

quality-controlled and traceable calibration chain from a primary standard held at the CCL to the transfer standards available at the World Calibration Centre (WCC).

4.2 Primary ozone standard

Ozone is amongst a set of trace gases for which, due to their reactivity, no material standard (e.g. ozone in air mixture) can currently be prepared and stably stored. Therefore the primary standard is an ozone photometer and traceability is ensured through instrument comparisons.

The U.S. National Institute of Standards and Technology (NIST) is the Central Calibration Laboratory for the surface ozone measurements in the GAW Programme. NIST provides a primary standard for ozone measurement through a Standard Reference Photometer (SRP⁴). The SRP operates by generating an ozone-rich atmosphere, within a stream of dry air that was previously without ozone. One part of this ozone rich air stream flows through the SRP, which measures the ozone mole fraction in an absolute sense based on the absorption of the gas using a known UV cross section, the absorption path length, gas temperature and pressure. Calibration of another instrument is accomplished by flowing another fraction of the ozone rich air stream through that instrument, comparing the mole fraction measured by the SRP to that measured by the other instrument, and calculating a calibration equation, which is usually a linear equation with a slope and intercept and their stated uncertainties.

GAW has adopted the SRP manufactured by the National Institute of Standards and Technology (NIST) as the primary standard for measurements of surface ozone within its network of sites. NIST has manufactured SRPs since 1983, and all SRPs are replicates of the first instrument SRP0. NIST maintains two of these (SRP2 and SRP0) within its own laboratories. The others (48 replicates as of 2011) have been sold worldwide (see <http://www.nist.gov/mml/analytical/gas/srp.cfm>).

4.2.1 Principle of measurement and the associated uncertainty of the NIST-SRP

The measurement of ozone mole fractions by an ultraviolet absorption primary reference photometer is based on the absorption of radiation at the atomic emission wavelength of mercury vapour of 253.7 nm by ozone in the gas cells of the instrument. This is the same technique that is recommended for ozone analyzers at GAW measurement stations (see Section 6). All SRPs use the same conventional value of the ozone absorption cross-section based on the measurements made by *Hearn (1961)*. The instrument has dual cells where ozone-rich air and ozone-free air are simultaneously measured in the two cells and then the air streams swapped to repeat the measurements. One aspect of the instrument design that uses two gas cells is that it minimizes the influence of the instability of the light source. The measurement equation is derived from the Beer-Lambert and ideal gas laws. For consistency in international discussions, the nomenclature used here is copied from that utilized by BIPM (*Viallon et al., 2006a*).

The number concentration (C) of ozone is calculated from:

$$C = \frac{-1}{2\sigma L_{\text{opt}}} \frac{T}{T_{\text{std}}} \frac{P_{\text{std}}}{P} \ln(D) \quad (1)$$

where

σ is the absorption cross-section of ozone at 253.7 nm under standard conditions of temperature and pressure. The value used is: $1.1476 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ (ISO, 1998).

$\ln(D)$:

L_{opt} is the optical path length of one of the cells

⁴ It is important to note that the term SRP in this document applies only to ozone standard reference photometers either manufactured by NIST or manufactured to their specifications under their oversight

T_{mes} is the temperature measured in the cells
 T_{std} is the standard temperature (273.15 K)
 P_{mes} is the pressure measured in the cells
 P_{std} is the standard pressure (101.325 kPa)
 D is the product of transmittances of the two cells:

$$D = T1 \cdot T2 \quad (2)$$

with the transmittance (T) of one cell defined as

$$T = \frac{I_{ozone}}{I_{air}} \quad (3)$$

where

I_{ozone} is the UV radiation intensity measured in the cell when containing ozonized air, and
 I_{air} is the UV radiation intensity measured in the cell when containing ozone-free air (also called reference or zero air).

Using the ideal gas law equation (see Section 3.1), equation (1) can be recast in order to express the measurement results as a mole fraction (x) of ozone in air:

$$x = \frac{-1}{2\sigma L_{opt}} \frac{T}{P} \frac{R}{N_A} \ln(D) \quad (4)$$

where

N_A is the Avogadro constant, $6.022142 \times 10^{23} \text{ mol}^{-1}$, and
 R is the gas constant, $8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$

The "2" in denominator of Equations 1 and 4 is a consequence of the fact that average transmittance has to be used: $0.5 \cdot [\ln(T1) + \ln(T2)] = 0.5 \cdot \ln(T1 \cdot T2)$

The formulation implemented in the SRP software is:

$$x = \frac{-1}{2\alpha_x L_{opt}} \frac{T}{T_{std}} \frac{P_{std}}{P} \ln(D) \quad (5)$$

Where α_x is the linear absorption coefficient under standard conditions, expressed in cm^{-1} , linked to the absorption cross-section with the relation:

$$\alpha_x = \sigma \frac{N_A}{R} \frac{P_{std}}{T_{std}} \quad (6)$$

A comprehensive analysis and explanation on the SRP uncertainties can be found in *Viallon et al. (2006a)*. The standard measurement uncertainty of a SRP is the combination of uncertainties which are proportional to the ozone mole fraction (eq. 5), e.g. to the gas pressure P , gas temperature T , light path length in the gas cells L_{opt} and ozone absorption cross-section σ , together with the uncertainty of the ratio of light intensities D which is constant and can be seen as the instrument noise. The standard uncertainty of the common SRP of the comparison BIPM.QM-K1 (SRP27), in the range 0-100 nmol mol^{-1} goes from 0.28 nmol mol^{-1} to 1.13 nmol mol^{-1} if all contributions to the uncertainty budget are included, and from 0.28 nmol mol^{-1} to 0.40 nmol mol^{-1} if the contribution from the ozone absorption cross-section is omitted.

4.2.2 Absorption cross-section for ozone

The linear absorption coefficient under standard conditions α_x used within the SRP software algorithm is 308.32 cm^{-1} . This corresponds to a value for the absorption cross section σ of 1.1476

$\times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ (rather than the more often quoted $1.147 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$). In the comparison of two SRP instruments, the absorption cross-section can be considered to have a conventional value and its uncertainty can be set to zero. However, in the comparison of different methods or when considering the complete uncertainty budget of the method and to ensure SI traceability, the uncertainty of the absorption cross-section should be taken into account. A consensus value of 2.12% at a 95% level of confidence for the uncertainty of the absorption cross-section has been proposed by the BIPM and the NIST (*Viallon et al., 2006a*). There is work underway to re-evaluate the cross-section value. Recent experiments conducted by the Gas Analysis Working Group of the CCQM/BIPM, with the BIPM taking the lead using a laser based system, show that the widely accepted value may be biased by as much as 3% (Petersen et al., 2012). This potential discrepancy would affect UV measurements as a possible bias, but would have no impact on the stability of the measurements over time.

4.3 World Calibration Centre for Surface Ozone (WCC-Empa)

Empa is designated by WMO as the World Calibration Centre for Surface Ozone (WCC-Empa). As a World Calibration Centre, Empa is responsible for maintenance of the laboratory and transfer standards for ozone that are traceable to the primary standard and the scale propagation to the measurements at the GAW stations. In 2010, WMO signed the Mutual Recognition Arrangement of the International Committee for Weight and Measures (CIPM-MRA), and designated Empa to represent WMO under this MRA for Surface Ozone measurements. This enables Empa to participate in the BIPM-coordinated key comparisons (BIPM.QM-K1) and to demonstrate their degree of equivalence with the NIST SRP.

WCC-Empa currently maintains two Standard Reference Photometers, SRP15 and SRP23, and uses a transfer standard (TS) for on-site comparisons during performance audits at GAW stations. WCC-Empa also provides an essential link to a primary standard in cases where GAW stations are unable to link directly to the CCL. Further description of the work of the WCC-Empa is given in Section 9.

Key comparisons can be used as a mean to evaluate the uncertainty of the primary standard provided for the GAW Programme. The degree of equivalence of all ozone standards is determined against SRP27 maintained at the BIPM that acts as a common reference for the ongoing comparisons. Analysis of the results for SRPs in the BIPM.QM-K1 comparison for the years 2007-2011 show a standard deviation of $0.14 \text{ nmol mol}^{-1}$ in the degrees of equivalence values for standards compared at a nominal mole fraction of 80 nmol mol^{-1} . By comparison the standard uncertainty of a SRP at the same mole fraction (see following section) has a typical value of $0.36 \text{ nmol mol}^{-1}$. Comparison of these uncertainties shows that the compatibility between measurement results from different SRPs is consistent with that expected from the uncertainties in individual SRP measurements where there is an absence of bias between instruments.

Provided a SRP is well maintained, upgraded when advised by NIST, and regularly demonstrated to be in agreement with other SRPs, NIST and BIPM consider the SRP to be a primary standard. Therefore, there is no calibration of SRP instruments, only validation of functioning within defined characteristics. An underperforming SRP must be evaluated for internal degradation of optics, drift in electronic components, or other physical problems and the comparison repeated until the SRP performance is verified.

The WCC-Empa has compared its SRP against the BIPM SRP in 2004 and 2012. In 2012 the report (*Viallon et al., 2012*) recorded that "this comparison indicated very good agreement between the two standards".

GAW measurements must be traceable to the WMO-assigned standards and scales. The WCC-Empa, as stated earlier, performs regular calibrations and performance audits at GAW sites using transfer standards. This is the route by which most GAW stations receive their calibration and by which all are audited. This is discussed in more detail in Section 9.

5. SELECTION OF MEASUREMENT TECHNIQUES FOR MEASURING TROPOSPHERIC OZONE AT GAW STATIONS

Ozone measurement techniques suitable for deployment at GAW stations need to fulfil several requirements:

- The instrument's signal-noise ratio, limit of detection, and stability must be appropriate, given current technology, either to meet, or if that is not possible, to approach the data quality objectives described in Section 3
- The instrument must be free of interference, or interferences must be well characterized so that the DQOs can be either met, or if that is not possible, approached
- The measurements must be traceable to the primary calibration standard at the CCL (Section 4)
- The instrument must be deployable at locations with possible limited supply of power and compressed gases, and it should require little presence of an observer on site
- Resource requirements and costs must not be prohibitive.

After consideration of these factors (see review of measurement techniques in Annex C), it is recommended to use UV absorption as the routine measurement technique for continuous in-situ tropospheric ozone observations in the GAW Programme. GAW stations with extended research programmes are encouraged to experiment with other in-situ ozone measurement techniques. Currently, cavity ring-down spectroscopy appears as a potentially attractive method which may be able to fulfil the requirements in terms of accuracy, stability, power consumption, and robustness in the future.

In addition, GAW stations with extended research programmes are encouraged to add remote sensing techniques that have the potential to link near-surface and satellite-based tropospheric ozone data.

6. ULTRAVIOLET ABSORPTION TECHNIQUE FOR MEASURING TROPOSPHERIC OZONE

6.1 Theory

The measurement of ozone mole fractions by an ultraviolet absorption ozone analyser is based on the absorption of radiation at 253.7 nm by ozone in the gas cells of the instrument. There are two types of configurations for these instruments. Some instrument designs have a single cell where ozone-rich air and ozone-free air are sequentially measured in the same cell. Other instrument designs have dual cells where ozone-rich air and ozone-free air are simultaneously measured in the two cells and then the air streams swapped to repeat the measurements and the ozone measurements from the two cells are averaged. One aspect of the instrument design that uses two gas cells is that it negates the influence of the instability of the light source. The ozone-free air is obtained by diverting part of the sample air through an ozone scrubber which destroys or removes all the ozone from the part of the air stream passing through the scrubber⁵. The measurement equation is derived from the Beer-Lambert and ideal gas laws and is presented in Section 4. The definitions of symbols are not repeated here.

As explained in Section 4, the mole fraction x of ozone in air is calculated with the following equation:

$$x = \frac{-1}{2\sigma L_{\text{opt}}} \frac{T}{P} \frac{R}{N_A} \ln(D) \quad (7)$$

The assumptions inherent in using this equation to derive ozone mole fraction from an ambient ozone photometer are examined in the following sections.

6.2 Limitations of ultraviolet monitors for measuring ozone in ambient air

An ultraviolet absorption ambient ozone analyser (OA) is in principle an absolute instrument, provided all the requirements of equation (7) above are met. However, in practice this may not always be the case. A description of typical components of an ozone photometer and its characteristics can be found in the ISO standard 13964:1998 (ISO, 1998). The specifications for operation of an ozone photometer as an ambient ozone analyser presented in these Guidelines are more stringent, as it is necessary for long-term measurements in the global atmosphere.

The assumptions inherent in using equation (7) to measure ozone in ambient air that may be compromised are that:

- The light detected is purely 253.7 nm
- The light beam is collimated and passes directly through the cell
- The light path length L_{opt} is well defined (L_{opt} will differ from the cell length in many cases)
- The ozone absorption coefficient is known and its uncertainty is evaluated
- The pressure is measured with a defined uncertainty and any difference between the pressure of ozone-rich air and ozone-free air is minimized and its effect on the ozone measurement is evaluated
- The temperature of the ozone sample is measured with a defined uncertainty and any gradient of temperature within the instrument gas cell(s) is minimized and its effect on the ozone measurement is evaluated
- The ozone is completely removed in the ozone-free air stream
- The sample (either ozone-rich air or ozone-free air) is distributed completely throughout the cell prior to the commencement of measurement (sufficient flushing time)

⁵ An ozone scrubber is an in-line device through which the sample air can flow. The ozone scrubber contains a chemical, usually a catalyst, which selectively destroys the ozone and should not affect the other constituents in the air sample

- There is no destruction or creation of ozone either within the cells or within the gas routing system between the introduction of the sample and the cells, apart from within the specific unit (ozone scrubber) designed to remove ozone from the sample stream
- Any differences in the optical transmission of the cells between measurements of ozone-rich air and ozone-free air are due to the effects of ozone alone, i.e. the measurement is free of interferences.

These assumptions are examined in the subsequent discussion.

Meyer et al. (1991) examined the spectral characteristics of the low-pressure mercury lamps used in ozone analysers. When the spectral characteristics of the lamp, the cell transmission and the detector response were combined, 98.8% and 99.2% of the light response of the photodiode is due to light in the 250 to 259 nm region. The ozone absorption coefficient varies across the region 200 to 320 nm and so a small bias will be introduced into the measurement depending on what fraction of the UV radiation is not in the line at 253.7 nm. This presence of light at other wavelengths may be more critical when considering interferences.

The assumption made is that the light beam is collimated and passes directly through the cell. *Meyer et al. (1990)* reported reductions of 82% and 86% in the amount of radiation being detected when the cell walls were removed. Consequently the assumption of a collimated beam is incorrect. The light path must involve scattering from the cell walls. Calculation shows that the additional path length is approximately 0.05%. However the fact that 80% of the light scatters off the cell walls makes the measurement very sensitive to variations in the scattering properties of the cell walls. The effect of water vapour within the cells appears to change the scattering and absorption properties of surfaces within the cell and thus to create an apparent ozone signal (*Meyer et al., 1991; Wilson and Birks, 2006*). Multiple reflections on the cells windows and other optical components can also occur, as demonstrated in the original version of the NIST SRP (*Viallon et al., 2006a*). An underestimation of the total path length of the order of 0.5% was evaluated in that case⁶. In the case of commercial ozone monitors with the characteristics described above, the determination of the optical path length is complex and the method of determination is not provided with the instrument documentation.

The uncertainty in the ozone absorption coefficient at 253.7 nm is evaluated at $\pm 2.12\%$ (at 95% level of confidence) (*Viallon et al., 2006a*). This is a limitation on the accuracy of the measurements.

The methods for establishing the temperature and pressure in the cells of typical commercial ozone analysers are, in some cases, not explicitly described in detail in the instrument manuals. Pressure is normally measured in only one cell. There can be substantial differences in measurements near the cell and in the cell. Errors of 10 hPa (~0.8 Torr) in the pressure measurement translate to an ozone correction of 0.1%. The temperature of the air in the optical cell is determined, in some commercial instruments, as the temperature of the optical bench. Errors of 3 to 4 °C in temperature correspond to a 1% error in the ozone measurement. These effects have been studied and dealt with in NIST SRPs (*Norris et al., 2008; Viallon et al., 2010*), but have not been systematically reported for commercial ozone analysers.

The cell needs to be flushed with at least three times its volume of sample air after the mode switch and before the measurement commences. As pump components age, pumping rates can decline. This issue could cause an underestimate in ozone concentration. In some instruments the time required for this flushing is ~ 2 seconds at operational flow rates.

In rare circumstances the ozone scrubber can lose its efficiency. Either regular checks should be made to ensure that the ozone scrubber retains 99.9% ozone destruction efficiency, or,

⁶ The total path length was corrected in an upgraded version of the NIST SRP (*Norris et al., 2008, Viallon et al., 2010*).

if the tests cannot be done, routine replacement of the ozone scrubber should be undertaken. The ozone scrubber operating at an efficiency of 99.9%, at an ambient ozone mole fraction of 30 nmol mol⁻¹, will transmit 0.03 nmol mol⁻¹ ozone, causing a negligible measurement bias.

Ozone destruction can take place within the sample paths of an ozone analyser on occasion. *Zucco et al. (2003)*, in a systematic study, measured an ozone loss of 1.1% in a commercial ozone photometer. Regular maintenance and cleaning should minimise this. The use of a second ozone analyser and a calibrator provides the means that a direct measurement can be made of this ozone loss within the analyser with the right experimental design. It is also possible that the solenoid valves that switch the zero and sample air between the two cells leak. This leads to an apparent ozone amount that is diminished compared with the correct amount. Regular leak checks on these solenoids are essential.

The final consideration here is whether the measurement of absorption difference between the cells of the photometer is due to ozone alone or other causes. If there is a measured difference between the zero and sample, it appears as an ozone signal. There are three potential causes of such interference, namely, electrical, physical and chemical. For instance there could be an electrical interference from the solenoids on the photodiode circuits that is synchronised with the sample/zero cycle that appears as a zero offset. *Proffitt and Mclaughlin (1983)* discusses such interference. Measurement with zero air in both cells and the flow off should detect this. Pressure and temperature differences between the cells in zero and sample mode combined with Raleigh scattering will cause differential attenuation of the UV light beam in all the cells (*Ityaksova et al., 2008*), but provided the pressure and temperature differences between the cells are minimised within 1%, this will not cause a spurious ozone signal >0.1 nmol mol⁻¹. Chemical interference will occur via the role of the ozone destroying scrubber. This scrubber can act as a buffer reservoir for both H₂O and other UV absorbing substances. When ambient humidity changes, or the concentration of the other UV absorbing substances changes, the scrubber can either take up or release both H₂O and these other substances from or into the zero air line and the consequence is a spurious ozone signal. There are compounds other than ozone that absorb at 253.7 nm and the other wavelengths present in the optical system of the ultraviolet ozone analysers. These include mercury, some aromatic and halocarbon compounds (*Grosjean and Harrison, 1985*); aerosol (*Jacobson, 1999*), and water vapour (*Tikhomirov et al., 1998*). *Tikhomirov et al. (1998)* gives an absorption coefficient of H₂O of 2.3 X 10⁻⁹ cm⁻¹ Pa⁻¹ at 255 nm. Thus the absorption of water vapour in air saturated at 20 °C would be equivalent to approximately 17 nmol mol⁻¹ O₃, a significant absorption. If the scrubber retains and releases water vapour, depending on the direction and extent of the change, a temporary spurious signal of up to 17 nmol mol⁻¹ is possible. Thus it is of importance to have scrubbers with minimum water uptake, and to allow adequate equilibration time when changing from ambient measurements in moist air to a dry air calibration and vice versa. This effect is further confounded if the cell walls change their reflectivity depending on ambient humidity as discussed above and by *Wilson and Birks (2006)*.

There is a further aspect to this H₂O interference, via a pressure effect, that could occur when there are other significant UV absorbers or scattering agents within the gas phase that may be unaffected by the scrubber. Consider the case where the partial pressure of H₂O in the zero cell varies independently of that in the sample cell because of retention of H₂O by the scrubber. Because of the instrument design, both cells must have the same total air pressure. Therefore the incoming sample air is diluted relative to the zero air by the presence of water vapour within it relative to zero air. Likewise any UV absorbers within the sample air will be diluted relative to the zero air. This will cause an apparent negative ozone signal. (Release of H₂O vapour by the scrubber would cause an apparent positive ozone signal.) This phenomenon has not been specifically investigated so far but may account for part of the "H₂O interference effect". The effect described in this paragraph, is equivalent to a difference in pressure between the sample and zero air cells, and small pressure differences could cause similar erroneous readings. There is need for measurements of the transmittance of background air and laboratory air at these wavelengths (253-255 nm) and other wavelengths present in the ozone detection system, to evaluate this effect, as it may become significant with increasingly stringent surface ozone DQOs.

Other requirements for an absolute instrument are documentation traceable to primary standards of the measurements of length, pressure and temperature, and a combined uncertainty estimate.

Because of the above mentioned effects particularly the determination of the optical path length and the temperature of the air sampled, commercial ozone monitors are not absolute ozone monitors and therefore require calibration. It is recommended to have in place a schedule of regular checks, maintenance and calibration of ambient tropospheric ozone analysers at GAW stations including comparisons with standard reference photometers or transfer instruments (see Sections 4 and 8). Operators should strive to minimise all of the above mentioned effects for the purpose of maintaining a high level of stability of measurement in their ozone record.

6.2.1 An example of interference in ambient ozone measurements

An example of interference with ozone measurements is given in Figure 2 where the results from three ozone analysers during the passage of a smoke plume at Hohenpeissenberg Observatory, Germany are presented. The period of smoke is indicated by the particle count at the bottom of the plot. During the period 11:00 to 15:00 h on 7 February 2000 the sampling by two of the analysers at the Observatory, a UV monitor (red line) and a chemiluminescent monitor (green line) was within a smoke plume from a small forest fire. A third UV ozone analyser sampling at a location 150 m away (black line) was not in the plume and therefore unaffected by the smoke. This third instrument showed comparable ozone concentrations to those of the first two throughout the rest of the day, but not during the smoke event. All three instruments had 5 micron filters on their inlet lines that should remove the bulk of the smoke particles. The UV ozone monitor sampling the smoke (red line) shows a series of sharp peaks, generally greater than 10 ppb, corresponding to the passage of the smoke and correlated significantly ($r= 0.6$, $N= 360$) with the Aitken particles. The chemiluminescent ozone analyser (green line) shows a series of negative excursions, generally less than 10 ppb, corresponding to the passage of the smoke and anti-correlated significantly ($r= -0.25$, $N= 360$) with the Aitken particles. This shows how two instruments, generally specific to ozone can be affected by smoke, and one or both are giving false readings during measurements in the smoke plume. The measurement interference may be associated with either the particles or gaseous constituents in the smoke, or both.

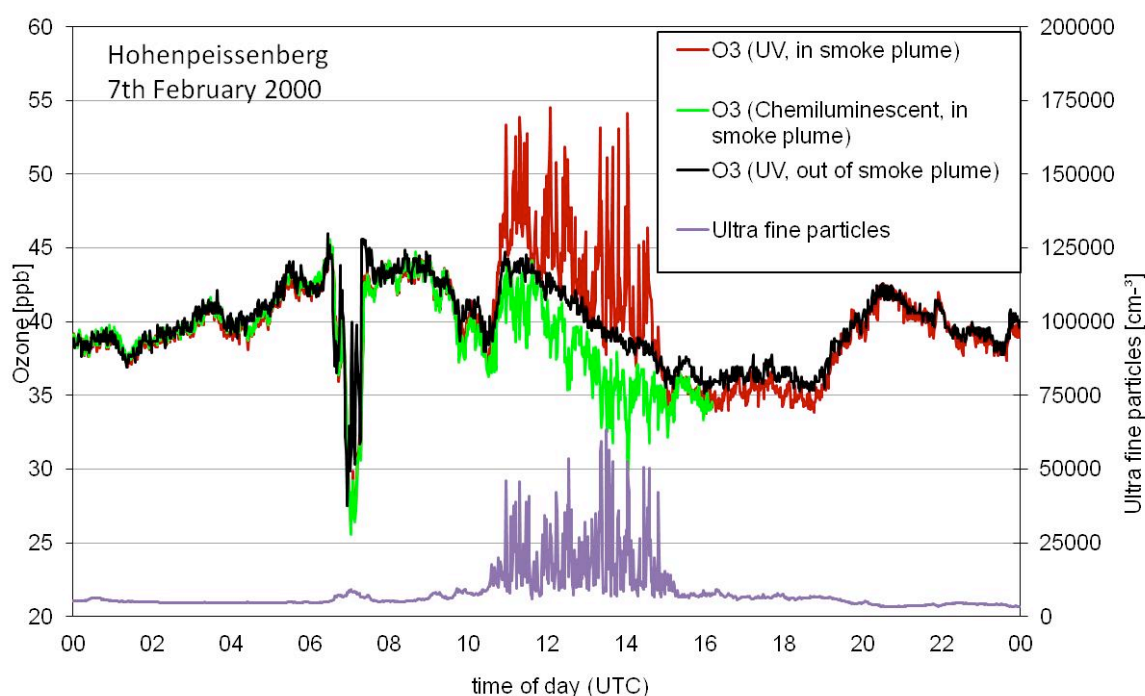


Figure 2 - Measurements of ozone at Hohenpeissenberg Observatory, Germany, 7th February 2000.
(Figure courtesy of Stefan Gilge, German Meteorological Service)

This example emphasizes the desirability for detailed comparison of measurements by instruments working with different detection principles particularly at GAW stations with extended programmes. For sites which are running only one ozone instrument, the data screening should be performed very carefully, e.g. by comparing ozone data with particle measurements, carbon monoxide, nitrogen oxides or other parameters.

6.3 Water vapour correction to ambient ozone mole fraction measurements

There is a role of H₂O in ozone measurement entirely independent of the interference described above. This is the mole fraction (mixing ratio) issue described here. Ultraviolet ozone analysers, because of their design, report ozone in ambient air in terms of mole fraction, typically parts per billion, with respect to moist air because the instrument measures the ozone density within its cell and the total pressure of the moist air. The fact that this measurement is done in respect to moist air is not often stated in reporting (see metadata of ozone records at WDCGG). *Schwartz and Warneck (1995)* acknowledge that atmospheric composition mole fraction (mixing ratio) values can be reported either with respect to dry air or with respect to moist air. *Schwartz and Warneck (1995)* state: "Since mixing ratio refers to the total gas mixture, the presence of water vapour causes the mixing ratio to vary with humidity. This variation may amount to several percent, depending on temperature and relative humidity. It is recommended that mixing ratio referred to dry air be reported provided that there is no loss in accuracy or precision associated with the conversion from mixing ratio referred to moist air. Mixing ratio referred to moist air is acceptable, however, and preferred if there would otherwise be loss in accuracy or precision due to the conversion."

The conversion from moist $x_m(\text{O}_3)$ to dry $x_d(\text{O}_3)$ mole fraction for ozone is, to an adequate approximation, given by:

$$x_d(\text{O}_3) = x_m(\text{O}_3) \cdot p_T / (p_T - p_{\text{H}_2\text{O}}) \quad (8)$$

where

p_T is the ambient pressure associated with the measurement

$p_{\text{H}_2\text{O}}$ is the partial pressure of water vapour associated with the measurement

Application of the conversion of moist mole fraction into dry mole fraction hence requires accurate water vapour observations. The measurements of water vapour would have to be co-located with the ozone measurements. The water vapour instrument would be required have a similar time response to the ozone instrument. The combined uncertainty of the water vapour measurements would have to be 1% relative to the maximum ambient water vapour mole fraction; that typically observed in moist tropical air.

The important aspects of this issue are that for comparison of surface ozone measurements with (1) ozone measurements in the upper troposphere and stratosphere, dry mole fractions are more relevant, because for the purpose of calculating mole fraction, the atmosphere at these heights is essentially dry and (2) ozone mole fractions in the output of chemical models are in dry mole fraction units.

The recommendations, presented in full in Section 3.1, are that (1) ozone measurements (where they were with regard to moist air) continue to be reported as mole fractions with respect to moist air and be accompanied by water vapour measurements, and (2) in all cases there be a clear statement of whether the ozone values refer to either dry or moist air mole fractions in the accompanying metadata.

Most current reports of mole fractions for surface ozone do not identify whether they are with respect to either dry or moist air, and probably are with respect to moist air. The difference may amount to about 4.3% under extreme conditions of 303 K and 100% relative humidity.

7. GAW STATION OZONE MEASUREMENT SETUP

The GAW Programme has two types of stations, Global and Regional stations (*WMO, 2007b*). There are also Contributing stations that belong to Contributing Networks (*WMO, 2011b*). The essential characteristics of a GAW Regional or Contributing Station include that the station location is such that, for the variables measured, it is regionally representative and is normally free of the influence of significant local pollution sources, as well as other requirements.

The essential characteristics of a GAW Global Station include that in addition to the characteristics of Regional or Contributing stations (*WMO 2007b; WMO 2011b*), a GAW Global station should: (1) measure variables in at least three of the six GAW focal areas; (2) have a strong scientific supporting programme with appropriate data analysis and interpretation within the country and, if possible, the support of more than one agency; (3) make measurements of other atmospheric variables important to weather and climate including upper air radio sondes at the site or in the region; (4) provide a facility at which intensive campaign research can augment the long-term routine GAW observations and where testing and development of new GAW methods can be undertaken (*WMO; 2007b*). At the GAW station, an observation made is of known quality and linked to the GAW Primary Standard. The data and associated metadata are submitted to one of the GAW World Data Centres (WDCs) no later than one year after the observation is made. Changes of metadata including instrumentation, traceability, observation procedures, are reported to the responsible WDC in a timely manner.

7.1 Facility requirements

Facility requirements include 24-hour available electricity and communications, a secure environmentally conditioned building suitable for the instruments and staff and ease of access. The facility and equipment should be suitable to sustain long-term observations with greater than 90% data capture (i.e. <10% missing data). The air sampling should be structured in a way to avoid local contamination sources. The laboratory building and inlet location on site should be set upwind of any other buildings, garages, parking lots, generators, other emission sources – any nearby areas where fossil fuels or biomass may be combusted and where intensive agriculture is undertaken. Station personnel should also remain downwind of the sampling laboratory and refrain from smoking as necessary. Within the facility, temperature control and clean lab environment are required. Instrumentation should not be exposed to sunlight.

7.2 Personnel requirements

Each set of measurements at a GAW station should be conducted under the guidance of a designated Responsible Investigator (RI). For tropospheric ozone, it is recommended that the Responsible Investigator have training in atmospheric chemistry, meteorology and atmospheric composition monitoring particularly as relevant to tropospheric ozone. There are requirements for technicians with skills in (1) analytical chemistry, particularly atmospheric composition monitoring as relevant to tropospheric ozone, (2) electrics and electronics, and (3) IT, particularly instrument control, data acquisition and data processing. It is recommended that station staff participate in the GAWTEC training programme and other GAW specialist activities where appropriate.

Provision should be made for back up staff to cover the periods when regular staff are away at training, leave etc.

7.3 Occupational health and safety

The tropospheric ozone programme includes use of equipment that can cause the following occupational health and safety issues:

- High ($1000 \text{ nmol mol}^{-1}$) mole fractions of ozone
- Ultraviolet radiation
- High voltages
- High-pressure gas lines (for example associated with the zero air generator)
- Noise
- Heavy and awkward equipment

Other hazards may occur. Appropriate occupational health and safety information, protective equipment and training are required.

7.4 Instrumentation requirements

The following instrumentation is required for a reliable long-term tropospheric ozone monitoring station under GAW:

- One ozone analyser (OA) is necessary. Experience at GAW Global stations favours the deployment of two ozone analysers for parallel measurements and multi-year overlap during instrument replacement where possible. These analyser(s) must be calibrated as recommended in Sections 3, 4, 6, 8 and 9 of these Measurement Guidelines
- Zero air supply that includes H₂O, VOC, O₃ and NO_x removal (pump/compressor, pressure regulator, charcoal scrubber, other scrubbers, drierite, 47 mm diameter, 5 micron PTFE filter)
- External or internal ozone zero and span check unit
- Ozone calibration source, known as a laboratory standard (LS), either at the station or bought to the station on regular occasions, traceable to the GAW primary standard (PS)
- Inlet line and filter both inert to ozone
- Instrument control and data acquisition interface
- Computer
- Internet connection/remote computer access
- Uninterruptable power supply

Equipment varies in specification and performance. There is some guidance in other parts of this document regarding equipment specifications for the ozone instrument and zero air generator. The WCC, existing long-running GAW stations and GAWTEC can provide advice on instrumentation that has performed successfully.

Manufacturers' instrument manuals should be available on site for all instruments used at the site.

7.4.1 Instrument replacement

Analytical instrumentation should be replaced every 7-10 years and IT equipment, because of its current rapid evolution, every 3-5 years depending on the availability of financial resources. With the two ozone analysers, one should be replaced every 5 years so that there is more than a year's overlap between ozone measurements from successive ozone analysers used at the station. The simultaneous data from the two analysers are valuable for QA/QC.

7.4.2 Instrument control and data acquisition software

A software system for data collection and quality assurance at GAW stations has been developed in a project under the Environmental Research Plan of the German Environment Ministry. In order to facilitate international standardisation of data processing at GAW stations, the software components are available to GAW stations free of charge. One component of the system that is recommended by the developers as a useful starting point is the programme "dafit", a data acquisition file integration tool. For further information contact the GAW Global Observatory Zugspitze/ Hohenpeissenberg.

7.5 Air inlet and sample lines

The air inlet is an essential component of the GAW monitoring system and any compromises made with regard to the inlet will affect all subsequent data. There are two key components of the inlet system, the location of the inlet and the materials of the inlet. In analytical chemistry terminology, the location of the inlet is an aspect of sampling and the passage of the air through the inlet corresponds to pre-treatment of the sample.

7.5.1 Location of the inlet

A key aspect of a GAW Station is that the measurements are "regionally representative and is normally free of the influence of significant local pollution sources," The height of the air sample

inlet is critical to this sampling of representative air. At some GAW stations the inlet is located 10 m above the roofline on the upwind (for background sampling) side of the building. Other GAW stations utilize a height of 2 to 3 m above the building roofline. Studies at Cape Grim (*Elsworth et al., 1985*) showed that there was significant ozone loss in light wind conditions at 3 m height compared to 10 m. This variation with height will be largest at sites in regions with vegetation and soil surfaces and smaller at sites surrounded by snow and water surfaces. New stations should, if possible, for a trial period sample ozone at 2-3 different heights to determine which inlet height is suitable. In the absence of such tests, it is recommended that new stations have inlets located, where practical, 10 m above the building roofline. GAW stations with extended programmes are encouraged to experiment with higher inlets that may provide observations representative of wider areas.

7.5.2 Inert materials for inlets and tubing

Ozone is an extremely reactive gas. Ozone deposition and reaction on the surface of different materials depends on the material type and the time of exposure of the ozone in the air stream to the material surface. Suitable inert materials must be utilized; these include both glass and fluorinated polymers. These fluoropolymers include polytetrafluoroethylene (PTFE), a synthetic polymer of tetrafluoroethylene, perfluoroalkoxy (PFA), a similar type of fluoropolymer and fluorinated ethylene propylene (FEP), a copolymer of hexafluoropropylene and tetrafluoroethylene. PFA and FEP have properties similar to PTFE but differ in being more flexible and capable of being heat moulded. FEP is softer than PTFE and melts at 260 °C; it is highly transparent and resistant to sunlight. PFA is commonly utilized as material with low reactivity to ozone (e.g. *Tanimoto et al., 2006*).

Inlet filters made of ozone-inert material (47 mm PTFE 5 micron filter) should be used prior to the analysers to prevent particulate matter from entering the analysers.

Materials that should not be used in contact with the air stream containing ozone include stainless steel, copper, rubber and poly vinyl chloride (PVC).

7.5.3 Physical/chemical design of the inlet and sample lines

Three different types of inlet are utilized at GAW stations and all three are acceptable. These are:

- One type of inlet is made of 50 mm o.d. glass (or even wider, up to 100 mm) that utilizes a high air flow to bring the sample air into a manifold within the laboratory. The residence time of the air sample within the glass inlet is typically <30 seconds. From the manifold a short length of inert tubing (PTFE, PFA etc.) connects the air sample stream to the instrument.
- A second type of inlet involves use of an inert material (PTFE, PFA etc.) inlet tube that has a rain shield at the external location and comes either direct to the instrument, or to a sample manifold nearby in the air sampling laboratory. These materials are inert to ozone and the air inlet should have a sufficiently short residence time so that negligible ozone from the free air stream can diffuse to and be destroyed at the inlet surfaces. Tubing diameters of 6 – 13 mm o.d. are used. A change to a wider bore ozone inert tubing should be made if the pressure drop in the tubing is >50 hPa.
- The third type of inlet is made of stainless steel, is 150 mm o.d., and has a laminar air flow (*Komhyr, 1983*). While contact with stainless steel can destroy ozone, this system is designed (*Komhyr, 1983*) with laminar air flow and a sufficiently short residence time so that the amount of ozone from the free air stream that can diffuse to and be destroyed on the inlet surfaces is negligible. Inlets of this type are suitable for sampling reactive gases and aerosol (*Komhyr, 1983*). For ozone, air is drawn from the centre of the inlet air stream via a short length of inert tubing (PTFE, PFA etc.) to the instrument.

7.6 Associated key measurements

Key measurements that will help in the interpretation of ozone measurements include those used for processing the ozone data, data selection and those related to ozone chemistry.

To process the ozone data and convert from mole fraction in moist air to mole fraction in dry air, the following parameters are necessary:

- Air temperature
- Air pressure
- A measurement of the water vapour in the air (one of: vapour pressure, dew point temperature, water vapour mixing ratio, relative humidity, wet-bulb temperature).

To understand the influence of nearby sources, to undertake data selection according to meteorological conditions and to quality control, the following additional parameters are useful:

- Wind speed and direction
- Particle number concentrations
- Carbon monoxide mole fraction
- Nitrogen oxides mole fractions
- Radon concentration.

To interpret the atmospheric chemistry processes affecting the observed ozone mole fractions, the following parameters are useful:

- Nitrogen oxides mole fractions
- Volatile organic compounds/CO/CH₄ mole fractions
- Water vapour concentration
- Air temperature
- Spectral distribution of solar radiation (suitable for determining molecular photolysis rates)/solar radiation.

Where tropospheric ozone measurements are undertaken at GAW stations, consideration should be given to measurement of these additional parameters. The measurement techniques for these parameters are presented in GAW Report No.143 Global Atmosphere Watch Measurements Guide (*WMO 2001b*) and in individual measurement guidelines (*WMO, 2007a; WMO, 2010b; WMO, 2010c; WMO, 2011a*).

7.7 Environmental issues that affect GAW stations and ozone observations

The environmental conditions/hazards that affect ozone observations include the following:

- Lightning strikes
- Hurricanes and other extreme weather
- Water condensation due to high humidity at high temperatures, particularly condensation in the sampling lines which can damage the instrumentation (e.g., Bukit Koto Tabang maintains a laboratory temperature of 27 °C to minimize these condensation issues)
- Inlet blockage at polar and high-altitude sites, due to ice riming and blowing snow
- Pollution events from electrical generators, nearby roads, agriculture, biomass burning etc.
- Access limited by environmental conditions such as flooding, severe weather etc.
- Lava flow for stations located on active volcanoes
- Tourist activities.

Consideration should be given to minimising the effect of the factors listed above where possible when setting up the station, while it is clear that the impact of natural hazards cannot be completely avoided.

8. GAW STATION OPERATING GUIDELINES FOR QUALITY OZONE OBSERVATIONS

8.1 System records

It is mandatory to keep a thoroughly maintained logbook. Raw data must be properly archived and managed at the station.

Each measurement site should have a field logbook. This should preferably be electronic and remotely accessible. The field log should contain any information which may be important for the interpretation of the measurement data.

Each measurement system, e.g. surface ozone, should further have its own (electronic) logbook. The instrument log should contain all information on instrument maintenance, calibration, failures etc. Normally there would be entries in the logbook at least weekly.

Each measurement system should also have an (electronic) check list, which is completed regularly. Alternatively (or in addition) instrument status information may be collected as part of the data acquisition. Instrument check lists should contain relevant instrument information such as lamp intensities, temperatures, flow rates, calibration factors, etc. (depending on instrument type).

Logbook records can be used as a basis for corrective actions if needed. Log entries (site and instrument) should be available when data are reviewed. QC procedures should include regular visual inspection of time series of the data and comparison with other available data (*WMO, 2003; WMO, 2009a*; see Section 10.6).

8.2 Regular quality control and instrument maintenance checks

All instruments should be maintained in accordance with their manufacturer's instructions and WMO Measurement Guidelines, following whichever is the more stringent. There should be a schedule (calendar) of checks and maintenance that are routinely performed at intervals of weekly, three-monthly, yearly and two-yearly.

8.2.1 Weekly checks and maintenance

The following checks should be performed twice per week and the results inspected and approved as satisfactory or else a corrective action undertaken. Criterion for acceptance should be based on the instrument manuals and these guidelines, see also sub-sections 10.4 and 10.6. Many of listed tests can be automated but the inspection of the results must still be performed by the operator:

- Sample inlet and plumbing inspection
- Instrument alarms
- Instrument sample air flows
- Lamp intensities
- Cell(s) pressure
- Cell(s) temperature
- Ozone ambient mole fractions
- Ozone reading precision
- Zero air and span checks
- Computer or data recorder time compared with a publicly available time server
- Data recording – are the ozone data being recorded correctly.

If the zero and span checks are automated, then it is recommended that they be performed daily.

8.2.2 Three-month checks and maintenance

The following checks should be performed once every three months (four times per year) and the results inspected and approved as satisfactory or else a corrective action undertaken:

- Leak check measurement system
- Clean measurement cell(s), check of inlet line for leaks
- Single point check of cell(s) pressure against ambient pressure with flow off
- Multipoint calibration of ozone instrument (OA) with calibrator (LS), (process as linear regression) as recommended in Section 8.6 of these Measurement Guidelines
- Examine the inlet particulate filter to determine if it is causing ozone loss. If necessary replace the filter
- If required, all glass and PTFE/PFA coated surfaces, cleaned with deionised water
- Examine the processed and quality controlled ozone data for the last quarter to confirm the satisfactory running of the instrumentation.

The issue of how often to change the particulate filter and how often to clean the inlet line may vary from station to station. Some stations change the filter at monthly intervals, some less frequently. At Cape Grim the filter is switched out of the sample line for 10 minutes every day, and from the sequence of measurements the ozone loss on the filter determined. These measurements show that in the Cape Grim environment, filter changing is only required yearly, or when intense fire smoke is sampled at the station. In other environments more frequent filter changes may be necessary; each station should determine its own requirement. Similar features will affect the requirement for inlet cleaning.

8.2.3 Yearly checks and maintenance

The following checks should be performed once per year and the results inspected and approved as satisfactory or else a corrective action undertaken:

- Audit of measurements including calibrations, zeros, spans, precision, ambient measurements, instrument parameters, records and logbooks
- Leaks within the analyser (OA), particularly in the switching solenoid;
- Ozone loss within the analyser
- Test efficiency of scrubber and if necessary replace
- Replace chemicals and filter in zero air source
- All glass and PTFE/PFA coated surfaces, cleaned with deionised water
- Measure the ozone loss in the inlet and the inlet filter. Replace the inlet if necessary
- Review the processed and quality controlled ozone data for the last year to confirm the satisfactory running of the instrumentation.

8.2.4 Two-yearly checks and maintenance

The following checks should be performed once every two years and the results inspected and approved as satisfactory or else a corrective action undertaken:

- Multiple point calibration of ozone analyser temperature sensor and pressure sensor
- Service OA at instrument manufacturer or at the station by a suitably trained technician/scientist
- Review the quality controlled ozone data and the calibrations for the last two years to confirm the satisfactory monitoring of ozone at the station.

8.3 Cleaning ozone instrumentation and inlet lines and testing

The requirement for cleaning the inlet lines and the instrument will vary according to the type of inlet, filters used and ambient environment of the station. Experience indicates that stations at high latitudes, high altitudes and in oceanic environments require very infrequent cleaning of the system perhaps yearly. The ambient ozone and air flow appears to passivate the surfaces including those with sea salt. However stations where soil dust or biomass burning smoke occurs will probably need a more frequent cleaning regime. This can only be determined by experiments including measurements of ozone inlet and filter losses at appropriate stations.

Testing for ozone loss in an inlet line plus filter is done using a calibrator feeding an excess of ozone rich air in at one end of the inlet plus filter and an OA measuring the ozone concentration at the other end. Prior to this the calibrator and OA are compared while connected with a short (1

m) FEP (or PFA) connection. Measurements at an elevated ozone mole fraction of 200 nmol mol⁻¹ allow for the detection of a 1% loss within the inlet and filter as a 2 nmol mol⁻¹ decrease. This is a suitable test.

Cleaning should not be undertaken unless necessary. Prior to use of tubing for air sample lines etc. there may be a need to clean them. Water soluble compounds can be flushed with deionised water. Organic material can be cleaned of surfaces with ethanol followed by flushing with deionised water. However this may not be normally necessary at all GAW stations. Following these treatments the lines/equipment should be flushed with 500 nmol mol⁻¹ ozone for several hours. Note the flushing gas should be vented outside the laboratory. Flushing sample lines and equipment with 500 nmol mol⁻¹ ozone is generally a satisfactory cleaning procedure.

8.4 Data acquisition and initial data processing

Data from the ozone instrumentation as well as the associated key measurements should be recorded with an adequate on-site data acquisition system. With modern instrumentation the data transfer will be digital via a connection method such as the RS232 standard or TCP/IP protocol. Digital data transfer allows the data to be transferred with the minimum possibility of corruption or modification. On older instruments analogue data transfer is utilized, and, with analogue, it is essential to have regular quantitative checks of the digital to analogue conversion in the instrument and the analogue to digital conversion in the data acquisition system. It is recommended to run the data acquisition on a computer with reliable internet connection for (automatic and near-real-time) data transfer and remote access.

The sampling frequency should be sufficiently high, i.e. in correspondence to the output rate of the analyser to achieve the best possible accuracy. Aggregates (1-minute) may be continually calculated by the data acquisition software. A common data acquisition system for a larger suite of trace gases and additional parameters can facilitate both station operation and preliminary data analysis. Besides the ozone readings, the data acquisition should also regularly (perhaps once daily for 10 minutes) record additional parameters including instrument status, lamp intensities, flow rates, pressure and temperature in the measurement cells, and any other key parameters.

As the raw ozone data are acquired, a flag should be attached to each data line to indicate it as uncorrected unvalidated data (see Section 10.2). The data acquisition system should allow the operator to instantaneously apply other flags to the data (e.g. during maintenance). The data acquisition system should also be coupled to instrument control so that when zeros, spans and calibrations are undertaken, the system automatically applies the appropriate flag to the data. Raw digital data are normally processed using the following algorithm (units in brackets):

$$X[I] = (UX[i] - ZA[i]) * CF / ICS, \quad (9)$$

where

CF is inlet correction factor required to correct for inlet loss (dimensionless)

ICS is instrument calibration slope which converts the instrument signal into mole fraction of ozone

ICS is determined from the instrument calibration with a traceable standard, i.e. the LS (instrument output unit)/(mole fraction)

ZA[i] is an average of the bracketing (or low-pass filtered) uncorrected zeros measured when a zero (blank) is applied externally to the instrument (instrument output unit)

UX[i] is uncorrected ambient measurements (instrument output unit)

X[I] is corrected ambient ozone, 60 second average, data (mole fraction).

The instrument output, also called signal or quantity value, is described in current metrology terminology as the indication of the measuring system (*Joint Committee for Guides in Metrology, 2012*). The instrument output unit typically will be volts for an analogue recording system and nominal mole fraction for a digital recording system.

As part of the initial data processing all periods recorded as invalid data in either the station log or the instrument log must be flagged as such. As the raw data are processed, the flag should be changed by the software from unprocessed unvalidated data to processed unvalidated data (see subsequent subsection).

8.5 Use of the slope and intercept settings in the ozone analyser

There is, within the electronics of many commercial ozone analysers, an ability to adjust the slope and intercept of the output signal to correct for the fact that the instrument may not read the same as the calibrator or transfer standard, for the reasons discussed in Section 6. The results from the Empa comparisons (*Klausen et al., 2003*) and experience at Global GAW stations indicate that the electronics of these analysers are more stable and less prone to drift than the development of other issues that cause calibration changes: drift of pressure and temperature sensors, increasing ozone loss in the instrument, filter and inlet, inefficient scrubbing, etc. Therefore it is recommended that after the initial instrument set-up the instrument hardware slope and intercept values are never changed. Any correction arising from the calibration is made via the processing software, see Section 8.4. In this way the data can be reprocessed easily if new information about factors influencing the ozone concentration and analyser response comes to light.

At the instrument setup, the slope and intercept can be either left on the factory settings, or preferably adjusted to 1 and 0. (In this use, the value 1 corresponds to the use of the ozone absorption coefficient of $1.1476 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ (ISO, 1998) in the instrument internal software.) Because the data processing (Section 8.4) incorporates the corrections in the external software, the selection of initial settings of slope and intercept is not critical.

8.6 Making zero and span measurements and filter checks along with ambient ozone observations

The ultraviolet ozone analyser can have a zero offset or intercept as discussed earlier. For ambient measurements, this intercept is measured by applying an external zero, such as introducing an ozone scrubber upstream of the inlet, and allowing ambient air to flow through the scrubber into the instrument. The instrument reads a non-zero reading (the intercept), generally $<1 \text{ nmol mol}^{-1}$. This zero intercept is an instrumental bias and is accounted for during data processing (Section 8.4). This external zero measurement should be performed with normal (moist) ambient air. If the zero check is made with dry air, interferences will disturb the measurement as discussed in Section 6.2. External zero measurements can be automated and made several times per week. If a dedicated ozone scrubber is used for this task, then the scrubber will equilibrate with ambient conditions, and only a few minutes will be required after inclusion of the scrubber in the air stream before zero air measurements are achieved (see Section 6.2).

Span checks are where an ozone generator is introduced upstream of the ozone monitor and a constant, but not well defined, ozone concentration is fed to the monitor. The result of this span check is to confirm that the ozone monitor is responding to ozone. Span checks are not calibrations as O_3 generators tend to be less stable than most of the analysers. Span checks only confirm that the instrument is responding to ozone and has not had a massive change in sensitivity. Span checks can be automated and made along with zero measurements several times per week.

Simple tests can be made on the inlet filter by temporarily removing it from the air inlet and comparing the average of the ozone concentrations observed before the filter is removed and after it is replaced with the concentrations while the filter is absent. This measures the loss (or lack of loss) of ozone on the inlet filter, and works successfully using ambient air. Filter checks can be automated and made along with span checks and zero measurements several times per week.

Alternately filter tests can be performed with a constant ozone source such as an ozone generator or ozone calibrator.

A simple system for automating the tests described above can be found in *Elsworth et al. 1984, 1985*. The system is described as an ozone monitor comparison system (OMCS) and includes a particle filter, an ozone scrubber and an ozone generator. The system is in-line and provides the monitors with filtered ambient air during normal monitoring. Once a day (or more often) the OMCS delivers to the monitors a sequence of zero air, air with ozone added from the generator, and finally unfiltered ambient air. This checks the operation of the ozone monitors and ozone losses on the inlet filter. The OMCS unit is designed with Teflon flow restrictors so that the pressure drop across the system (3 to 4 kPa) is independent of the mode in which the sequence is performed (*Elsworth et al., 1985*).

A schematic of such a system is shown in Figure 3. Air flows through Teflon tubing from the station air inlet on the left to the ozone analysers on the right. Air normally follows the path A, through the two Teflon 3 way solenoid valves and through the Teflon inlet filter. Once per day the solenoid valve V1 is activated and air flows along path B through the ozone scrubber and on to the analysers, providing the analysers with an external zero of un-dried ozone free air. After a satisfactory measurement period (15 – 30 minutes), the UV lamp is turned on and an ozone concentration is generated in the air stream. When the UV lamp is in a heated enclosure at around 50 – 60°C, a steady ozone generation rate is obtained. With the help of the adjustable shutter a suitable concentration can be obtained that is broadly repeatable from day to day, and a daily span check is possible. After the measurement of the span, the solenoid V2 is activated, and V1 kept activated, then the span measurement is made directly without the filter. After a satisfactory measurement period, the solenoid V2 is deactivated and a further span measurement made which allows, the ozone loss on the filter to be determined. At the end of this sequence both solenoids and the UV lamp are turned off.

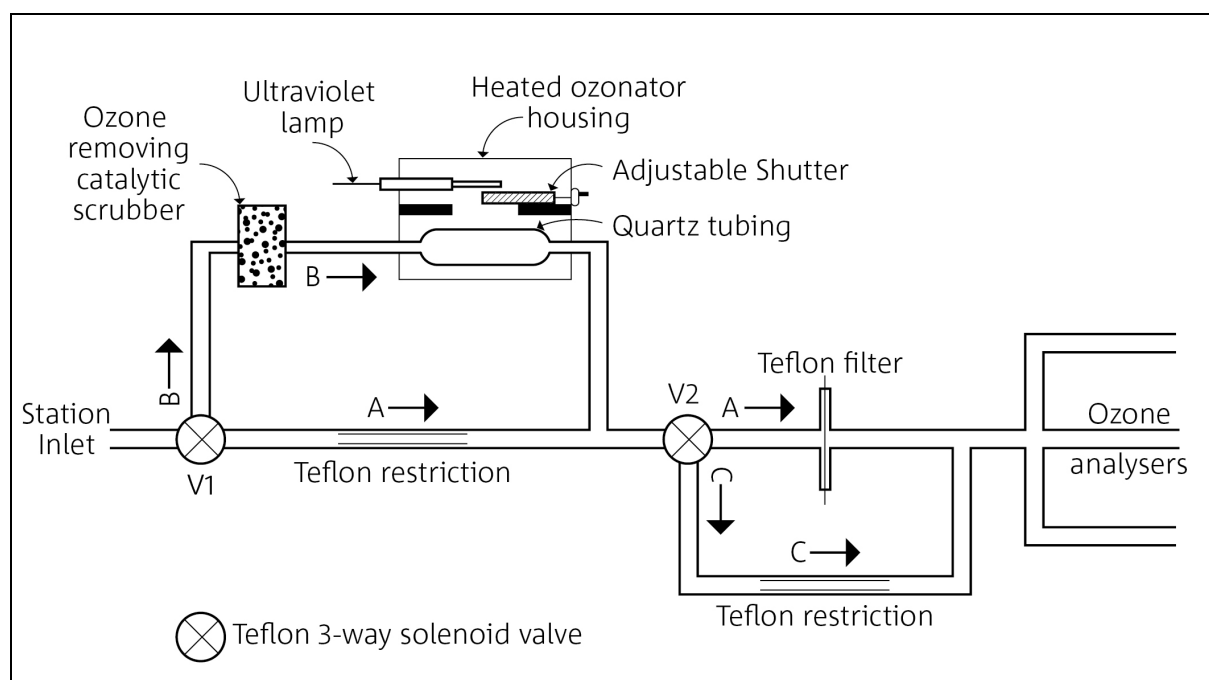


Figure 3 - A schematic representation of an ozone zero, span and filter check system.
(Figure courtesy of Ian Galbally, CSIRO Marine and Atmospheric Research)

8.7 Calibrating the station surface ozone analyser(s) with the station calibrator

The following calibration procedure is a modified form of the auditing procedure described by *Hofer et al. (1998)*, and procedures recommended by ISO (1998) and BIPM (2007). The equipment required are a station calibrator, also known as a laboratory standard (LS), station ozone analyser(s) (OAs) and zero air generator.

The zero air dryer specification is of an oil-free compressor utilizing ambient air that is dried and scrubbed with a system so that the mole fraction of ozone and nitrogen oxides remaining in the air are below detectable limits. The mole fraction of water in the zero air should be less than $10 \mu\text{mol mol}^{-1}$. The mole fraction of volatile organic hydrocarbons in the reference air should have a total less than $100 \text{ nmol mol}^{-1}$, with no mole fraction of any detected component exceeding 10 nmol mol^{-1} .

Before assembling the equipment for the calibration, check the instruments for leaks due to loose connections.

1. Assemble the calibration equipment consisting of the laboratory standard and zero air system. Position the LS as close as possible to the OA(s) in order to achieve short connections between the LS and OA(s). An example of the setup is given in Figure 4.
2. Prior to the calibration, all the instruments that will be used for the calibration shall be switched on and allowed to stabilise for at least eight hours. It is not necessary to turn on the zero air flow at this time, if the zero air pump can be turned on/off separately.
3. Check the pressure transducers of the LS and OA(s) compared to the current local barometric pressure (use station reference). This should be done when the flow is off, if the pump can be independently controlled. Otherwise additional experimental advice is necessary.
4. Turn on the zero air to the LS (if not already done). Make sure that the zero air flow through the cell(s) is sufficient so that an excess flow of at least 1 litre per minute through the vent(s) is guaranteed compared to the combined requirements of the photometers included in the calibration. Flush the cell(s) and the connection tubes by applying $500 \text{ nmol mol}^{-1}$ ozone for 2 hours (BIPM, 2007). This can be done during the instruments stabilisation period (Point 2 above).
5. Ensure that the LS data are being logged on the station acquisition system. Mark the data acquisition systems to indicate a calibration is being performed.
6. Disconnect the site OA(s) from the station's ambient air sampling manifold and connect it (them) to the LS ozone output port. Cap the sample port on the station's manifold.
7. A flow containing $500 \text{ nmol mol}^{-1}$ ozone is provided by the LS and is now drawn through the OA for at least 15 minutes. Make a note of the response time characteristics (fast/slow increase, quiet/noisy output signal).
8. Turn off the ozone generator of the LS. Allow the OA(s) and LS to sample zero air until a stable response is obtained, a minimum of 10 minutes is recommended. Now record a minimum of 10 consecutive values (30 s means) from the LS and the OA(s) appropriate to the instruments' interval of sampling reference and sample gas. The averages as well as the standard deviations of the recorded values will be evaluated. The two values are considered as valid if the associated standard deviation of the LS and OA measurements do not exceed 2 nmol mol^{-1} or 1.5% of the average value (which ever is the largest).
9. It is now necessary to generate at least five distinct ozone mole fractions that cover the ozone values recorded at the site. Recommended values are: marine sites: 10, 20, 30, 50, $100 \text{ nmol mol}^{-1}$ other sites as required (continental, elevated sites etc.): 10, 30, 50, 75, $150 \text{ nmol mol}^{-1}$. Use of a randomized order is recommended to capture variability due to any hysteresis effects in the instruments.
10. Adjust the LS ozone generator to achieve the desired mole fraction of O_3 and allow the OA(s) and LS to sample the air stream until a stable response is obtained, a minimum of 10 minutes is recommended. Now record a minimum of 10 consecutive 30-second-mean values or for at least 5 minutes (appropriate to the instruments' interval of sampling reference and sample gas) from the LS and the OA(s). The averages as well as the standard deviations of the recorded values will be evaluated. The two values are

considered as valid if the associated standard deviation of the LS and OA measurements do not exceed 2 nmol mol^{-1} or 1.5% of the average value (whichever is the largest).

11. Repeat the steps 8 to 10 for zero and each mole fraction level twice more if an enhanced estimate of the uncertainty of the calibration is desired.
12. Calculate the mean value for the zero and each mole fraction level, for all involved instruments. Perform a regression analysis with the LS mole fraction as the independent value on the x-axis and the OA mole fraction as the dependent values on the y-axis. Record the slope, the intercept and either confidence limits or the correlation coefficient on the data sheet. In this case the value of the slope determined is the instrument calibration slope (see Section 8.4).
13. Calculate the mean offset and span setting for all involved instruments.
14. Do not adjust the offset and span settings of the OA(s). The corrections are made via the data processing algorithm. This is the most stable way to operate the measurement system.
15. After recording all data for the calibration, reconnect the OA(s) to the station sampling manifold and check for normal OA operation.
16. If two OAs are in operation, cross-check the ambient air ozone data. If only one OA is used, check the plausibility of the ozone concentration in ambient air based on experience (see Annex B for typical ozone levels).
17. Make a note of the calibration stop time on the station data acquisition system.
18. Compare the calibration results to previous calibration results and WCC audits (if you had any) and to the target data quality objectives and determine the conformance to these DQOs.
19. Discuss the calibration results with the site operator and if necessary talk about any major deficiencies found and any corrective action required.

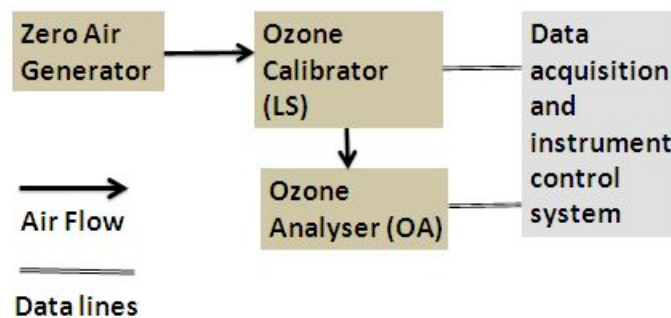


Figure 4 - The plumbing and data connections for the calibration at the GAW station

9. QUALITY ASSURANCE AND QUALITY CONTROL

9.1 Introduction

The goal of GAW measurements is to produce long-term records of known quality that are adequate for their intended use. Hence it is imperative that the measurement activities be quality-assured and the data be quality-controlled. Section 8 described the procedures for maintaining high-quality observations at the GAW station. This chapter presents the wider framework for Quality Assurance/Quality Control (QA/QC) of the GAW tropospheric ozone programme.

9.2 Calibration

9.2.1 Hierarchy of standards

All in-situ methods used to measure surface ozone have to be regularly calibrated with gases containing known amounts of ozone. Stations measuring surface ozone should have (or have access to) an ozone laboratory standard, LS (commonly called an ozone calibrator), with traceability to a SRP maintained by the WCC-Empa or the CCL (NIST). The process is outlined in Figure 5.

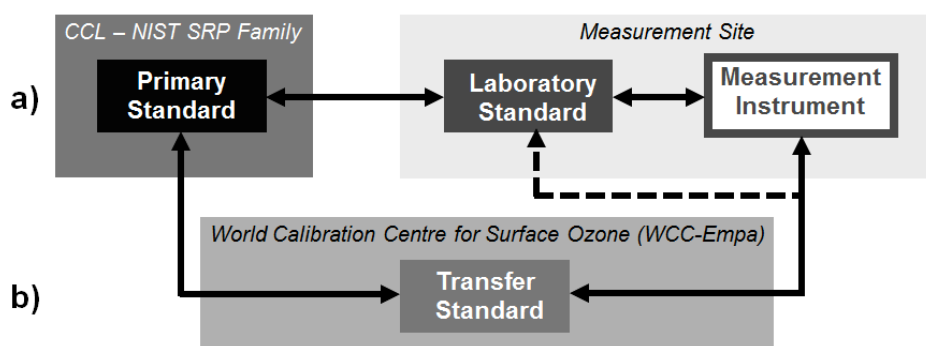


Figure 5 - (a) General traceability chain from the primary standards (NIST SRPs) to atmospheric observations (measurements) at GAW sites. (b) Independent assessment through system and performance audits carried out by the World Calibration Centre. Arrows indicate regular comparisons. Modified from *Buchmann et al. (2009)*

9.2.2 Audit Procedures

Empa – co-sponsored by MeteoSwiss – has operated the World Calibration Centre for Surface Ozone (WCC-Empa) since 1996 as a Swiss contribution to the GAW Programme. Under this mandate WCC-Empa is responsible for verifying the traceability of measurements to the designated reference within the GAW Programme. This is implemented by system and performance audits, as illustrated in Figure 5 (*Buchmann et al., 2009; Klausen et al., 2003*). According to the GAW Strategic Plan, a performance audit is defined as a voluntary check of conformity of a measurement where the audit criteria are the data quality objectives (DQOs) for the parameter under review (*WMO, 2007b*). A system audit is more generally defined as a check of the overall conformity of a station with the principles of the GAW quality assurance system. A more detailed description of a performance audit procedure can be found in *Hofer et al. (1998)*.

A schematic diagram showing the traceability of standards and the scope of a performance audit is shown in Figure 6. Regular inter-comparisons and re-calibration (arrows) of the laboratory standards (LS) against the primary standard (PS) maintained by the Central Calibration Laboratory (CCL) ensure traceability. The purpose of an audit is to verify this traceability by conducting an inter-comparison exercise with a travelling or transfer standard (TS) that is from the World Calibration Centre (WCC). At the station, the LS should be used for calibration of instrumentation. With reference to the time scale shown in Figure 6: the CCL NIST SRP family and WCC Primary Standard are compared every few years; the WCC audits a Station every few years; the WCC Transfer Standard is compared with the WCC Primary Standard within a few weeks before and

after each audit, and the WCC Primary Standard is again compared with the CCL NIST SRP family every few years.

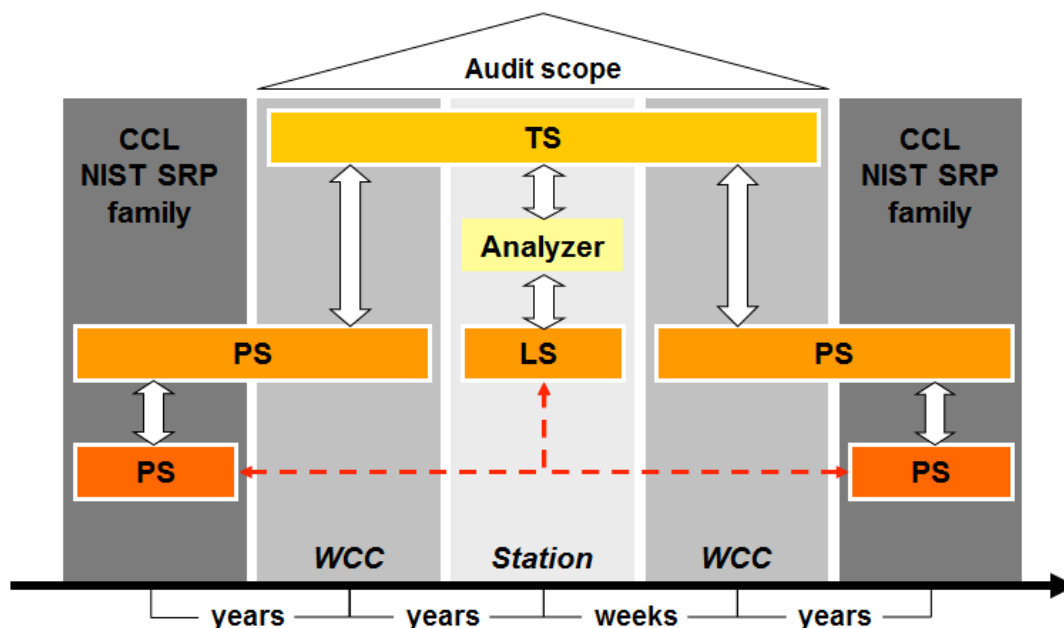


Figure 6 - Schematic diagram of the traceability of standards and the scope of a performance audit. LS is a laboratory standard either in the WCC or the Station; PS is the primary standard maintained by the Central Calibration Laboratory (CCL), TS is a transfer standard that is maintained by the World Calibration Centre (WCC). The red dashed lines indicate direct comparisons of a station laboratory standard with an SRP. The intervals between comparisons are indicated on the bottom scale. (Figure adapted from Buchmann *et al.* (2009))

In addition to the WCC, Regional Calibration Centres (RCCs) offer calibrations and traceability to the GAW reference on a regional scale. Currently there is only one RCC, the Regional Calibration Centre for Surface Ozone for the WMO Region III (South America) hosted by the Argentinean Weather Service in Buenos Aires. This RCC conducted the VI inter-comparison of tropospheric ozone analysers in South America in 2010. This regional inter-comparison included instruments from Chile, Uruguay, Paraguay, Brazil and Argentina. The standard instrument with traceability to the GAW reference (transfer standard = ozone calibrator) was provided by WCC-Empa (Switzerland).

At times GAW stations may have to wait for a WCC-Empa performance audit, which are infrequent as only approximately 4 stations are audited per year. These GAW stations may also not have a RCC, as only one exists. In this circumstance, a calibration of the station LS should be obtained from another NIST SRP that participates in the NIST/BIPM intercomparisons ([BIPM.QM-K1](#)), if available. The GAW station LS calibration will then be confirmed at the next WCC-Empa audit.

9.3 Evaluation of overall measurement uncertainties

All measurement data must be associated with a corresponding uncertainty. The uncertainty largely depends on the measurement technique and the realisation of the measurement itself, including the design and operation of the complete analytical system. Due to the individuality and complexity of different analytical set-ups, each laboratory must assess the uncertainty of its own specific system. The following briefly discusses contributions to the overall combined standard uncertainty of the measurements. Depending on the realisation of a specific measurement, additional contributions to the uncertainty need to be considered. Uncertainty estimates should be derived and expressed according to international standards (*Joint Committee for Guides in Metrology, 2008*).

In essence, the *combined uncertainty* of a measurement contains contributions due to the sampling, the calibration scale, the transfer of the calibration scale to the instrument, the repeatability (short-term variability) of the instrument, the reproducibility (longer-term variability, including drift) of the instrument, and uncertainty introduced during data processing. Not all of these components can be clearly separated, e.g., uncertainty due to the transfer of the scale is linked to the limited repeatability and reproducibility of analytical equipment and the distinction between some components is somewhat arbitrary. In general, these contributions are independent, and therefore, the combined uncertainty is the square-root of the sum of the squared individual contributions. When the input quantities contain dependencies, terms containing covariances should account for this. These covariances may increase or decrease the combined uncertainty. Uncertainties of measurements should always be reported with a statement of the *confidence level* or *coverage factor*.

All analytical techniques for tropospheric ozone measurements require calibration using a standard instrument and an ozone generator. Each calibration results in new instrument calibration factor(s) (zero and span for linear instruments) that are used in the data processing. Because only a limited number of calibrations are carried out, each single calibration may result in a bias to the true but unknown calibration of the instrument. The contribution of the calibration uncertainty to the overall uncertainty can be estimated using the reproducibility of repeated calibrations provided that the instrument parameters are not adjusted following the calibrations.

Some measurement techniques require post-analytical data treatment, e.g. for the compensation of zero or span drift. Such corrections are associated with uncertainties, which need to be considered in the uncertainty budget.

In addition to the above factors, interferences and/or changing environmental conditions may further influence the measurements and consequently have an influence on the associated uncertainties. These influences are often difficult to assess, but should not be neglected for the uncertainty budget. In particular, the inlet and sampling system must be checked regularly for leaks and ozone loss. These and any other potential sampling artefacts need to be accounted for in the estimation of the uncertainty budget.

9.4 Example of a systematic uncertainty analysis

An example of an uncertainty assessment of the primary ozone reference (SRP), a travelling standard (TS) and an on-site ozone analyser (OA) was described by *Klausen et al. (2003)*. This approach is adopted here. The units used here are nmol mol⁻¹ (except for in Figure 7 which presents an existing analysis) as the analysis is an example for station Responsible Investigators to follow.

9.4.1 Uncertainty of the primary reference (SRP)

A recent study has presented the uncertainty budget for the measurement of ozone mole fractions with a bias-corrected SRP maintained at the BIPM (*Viallon et al., 2006a*).

The uncertainty budget can be translated into one equation describing the combined standard uncertainty as a function of the ozone mole fraction. The following combined standard uncertainty (u) for the mole fraction range of 0-250 nmol mol⁻¹ ozone was found (when SRP reading is given in nmol mol⁻¹):

$$u(SRP) = \sqrt{(0.28)^2 + (0.011 \times SRP)^2} \text{ nmol mol}^{-1} \quad (10)$$

or, when neglecting the uncertainty of the ozone absorption cross section

$$u(SRP) = \sqrt{(0.28)^2 + (0.00292 \times SRP)^2} \text{ nmol mol}^{-1} \quad (11)$$

The mole fraction dependent part of the uncertainty determined by *Viallon et al.* (2006a) (equation 11) is considerably larger compared to the work by *Klausen et al.* (2003) due to improved understanding of the uncertainties in SRPs.

The uncertainty of the ozone absorption cross-section is a significant contribution to the total uncertainty as discussed in Section 4.2.2. However, for compatibility within a network using only UV absorption instruments, the contribution of the ozone cross section can be neglected, since it is a conventional value which has the same effect (bias) to all measurements within the network.

9.4.2 Uncertainty of the transfer standard

If the on-site ozone analyser (OA) is not directly compared and calibrated against a SRP, transfer standards (TS) are used for the calibration of the OA. In principle, the uncertainty of a TS can be determined by analogy to the SRP. For this purpose, the individual uncertainty contributions of all parameters influencing the measurement result have to be considered.

Alternatively, the uncertainty of a TS can also be estimated by statistical means. For example, *Klausen et al.* (2003) analysed a large number of TS-SRP comparisons to assess the repeatability of TS measurements. The contribution of the instrument noise was assessed by pooling a large number of zero and span data, and the linearity over a range of 0-200 nmol mol⁻¹ ozone was calculated from the TS-SRP linear regression residuals, noting that no mole fraction dependence was evident in the data. The drift of the TS over the calibration period (comparison of the TS before and after OA calibration) was again estimated by analysing TS-SRP comparisons before and after the calibration of the OA. This was done by calculating the standard deviations of the differences in intercept and slope of the TS-SRP comparisons bracketing the OA calibration. The contributions of the repeatability and the drift were combined, and the following combined standard uncertainty of the TS was estimated:

$$u(TS) = \sqrt{(0.43)^2 + (0.0034 \times TS)^2} \text{ nmol mol}^{-1} \quad (12)$$

It should be noted that this uncertainty assessment is only valid for the specific TS under investigation and cannot be generalized; each data producer is requested to calculate their own uncertainty budget considering their own circumstances.

9.4.3 Combined standard uncertainty of the ozone analyser

The uncertainty budget of the ozone analyser can also be estimated by combination of the contributions of the individual uncertainty components. An example of an assessment for an ozone analyser operated in the Swiss National Monitoring network is given below. The individual contributions to the combined standard uncertainty were estimated by either experimental data, manufacturer specifications or, in cases where no data was available, by expert judgment. Table 1 summarises the uncertainty budget for the measurement of ozone mole fractions with an OA traceable to a SRP maintained at Empa. The uncertainty components have been combined according to the methodology proposed by the Joint Committee for Guides in Metrology (2008). The budget was calculated for typical operating conditions of the instrument (temperature of 298 K, pressure of 100 kPa). In comparison to a SRP, the ozone analyser can be adjusted by setting of the calibration factors; therefore, the individual components of the uncertainty are different compared to a SRP. For example, imperfect determination of the optical path length can be compensated by corresponding settings of the span factor; the uncertainty in the determination of the setting itself, however, is a contribution to the combined uncertainty, since deviation from linearity and a remaining calibration bias, which cannot be compensated, add to the overall uncertainty.

Table 1 - Example of an uncertainty budget of an ozone analyser

Component (<i>y</i>)	Source	Distribution	Contribution to $u(x)$
Imperfect calibration / linearity	Comparison between TS and OA	Rectangular	$0.0017 \cdot x^*$
Repeatability	Instrument stability	Rectangular	$0.0016 \cdot x$
Span drift	Instrument stability	Rectangular	$0.0040 \cdot x$
Zero drift	Instrument stability	Rectangular	0.17
Pressure P	Pressure measurement	Rectangular	$0.0002 \cdot x$
Temperature T	Temp. measurement	Rectangular	$0.0005 \cdot x$
H ₂ O interference	Interference in the UV		$0.0060 \cdot x$
Other interferences	Interference in the UV		0.6
Sampling loss (Inlet)	Inlet material, dirt	Rectangular	$0.0014 \cdot x$

* where x refers to ozone mole fraction

The uncertainty components described in Table 1 can again be combined into one equation:

$$u(OA) = \sqrt{(0.62)^2 + (0.0077 \times OA)^2} \text{ nmol mol}^{-1} \quad (13)$$

A conservative estimate of the total uncertainty can now be obtained by combining the uncertainties of the ozone analyser (13), the transfer standard (12) and the primary reference (11).

$$u(O_3) = \sqrt{(0.81)^2 + (0.0089 \times O_3)^2} \text{ nmol mol}^{-1} \quad (14)$$

or, including the absorption cross-section uncertainty

$$u(O_3) = \sqrt{(0.81)^2 + (0.0139 \times O_3)^2} \text{ nmol mol}^{-1}. \quad (15)$$

The above uncertainties were calculated for 1-h averages. The aggregation time has a direct influence on some components of the combined standard uncertainty (e.g. instrument noise, drift), whereas others are independent of averaging time (e.g. uncertainty of the absorption cross section). Therefore, it is important that uncertainties are calculated for each aggregation time.

The above example shows how an uncertainty can be estimated. The principles of the estimation of an uncertainty are described by the Joint Committee for Guides in Metrology (*Joint Committee for Guides in Metrology, 2008*). Since uncertainty estimates depend very much on the individual measurement set-up, they cannot be generalised, and each data provider is requested to assess their own uncertainty budget at times of the station audit by the WCC. All data must be accompanied by an uncertainty estimate, which should also be accessible in the corresponding data centres.

At a typical background ozone mole fraction of 30 nmol mol^{-1} the combined uncertainty (equation 14) translates into a combined uncertainty of $\pm 1.7 \text{ nmol mol}^{-1}$ (2 sigma). This is 70% larger than the DQO defined from the dominant science objective of GAW tropospheric ozone

measurements in Section 2.2. However, much useful information to support decisions can be obtained from stations that achieve current best practice and these Measurement Guidelines aim to present that best practice.

9.4.4 Experimental verification of uncertainties

Real-world comparisons between TS and OA from the Swiss National Air Pollution Monitoring Network between November 2005 and November 2011 were used to verify the uncertainty estimate made above. Figure 7 shows the results, i.e. the intercepts and slopes, of 296 ozone analyser calibrations with transfer standards. All data points represent results prior to any adjustment of the analysers. Calibrations are performed every three months. Due to logistical issues, the calibration in winter is skipped at some sites leading to six months intervals. It can be seen that the deviations from the transfer standard usually lie well within the limits defined by equation 14, which confirms that the above uncertainty estimate is reasonable. However, it has to be stressed that the calibrations of the ozone analysers with transfer standards do not cover all issues in the uncertainty analysis, such as inlet losses and potential interferences.

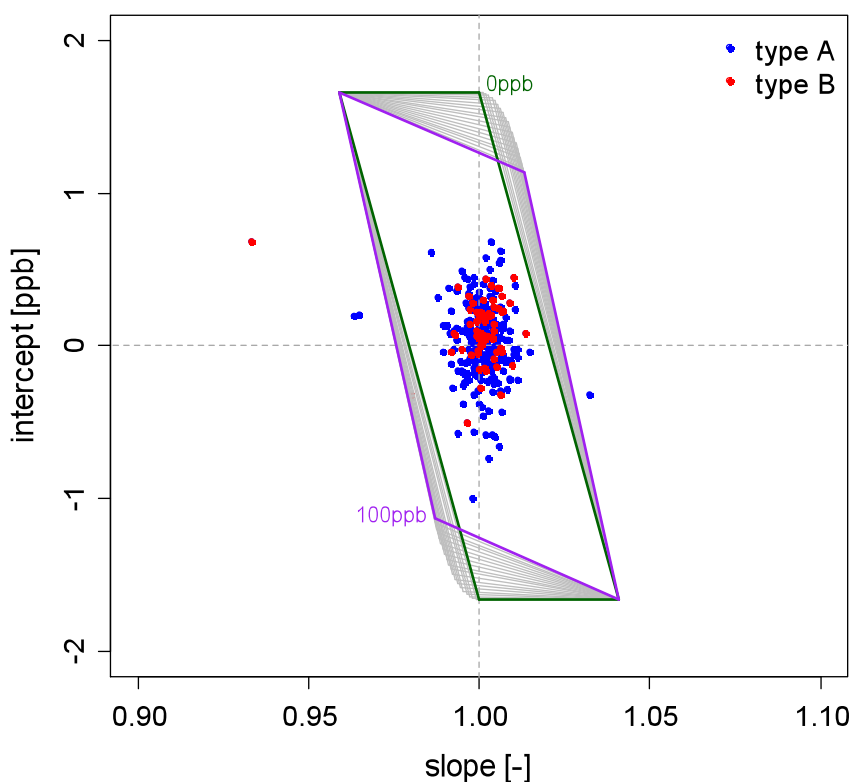


Figure 7 - Intercept vs. slope plot for 296 calibrations of various ozone analysers with transfer standards within the Swiss National Air Pollution Monitoring Network between November 2005 and November 2011 for two different types of UV absorption ozone instruments. The grey lines correspond to the uncertainties from Equation (14), expanded by a coverage factor $k=2$ for ozone mole fractions from 0-100 ppb. The uncertainties for 0 ppb and 100 ppb are highlighted in green and purple, respectively

10. DATA MANAGEMENT AND ARCHIVING

10.1 Introduction

These guidelines on data processing, management, and archiving describe current and emerging best practices with the key purposes to ensure that:

- The data reflect the measured atmospheric mole fractions of ozone to the best possible knowledge
- The data are free of errors
- The data are sufficiently documented to allow for meaningful scientific analyses
- User access to the data and combination with other data sets (e.g. other parameters from the same station, ozone records from different stations, model data, etc.) is as easy as possible
- The data can be used in quasi near-real-time for the evaluation of atmospheric forecast models
- The data are preserved for current and future use
- Information on the calibration and measurements conditions is preserved so that the quality of the data can be analysed retrospectively.

Figure 8 summarizes the main elements of the data flow as described in the following sub sections. Data acquisition and the initial processing (i.e. conversion of raw signals to mole fractions) have been described in Section 8.7. Section 10.2 summarizes the best practices of data processing and management, Sections 10.3 to 10.5 expand on this with a focus on automated software procedures which shall assist the station RI in the subsequent quality control and preparation of the data sets for archival at the WDCGG. These procedures allow, in parallel, for immediate use of the preliminary ozone data in near-real-time applications such as the evaluation of atmospheric composition forecast models, or data assimilation into such models. Sections 10.6-10.8 describe the necessary steps to quality control the data and for submission to the WDCGG. Section 10.9 lists best practices for dataset revision and re-submission, and Section 10.10 contains more information on the purpose and use of metadata.

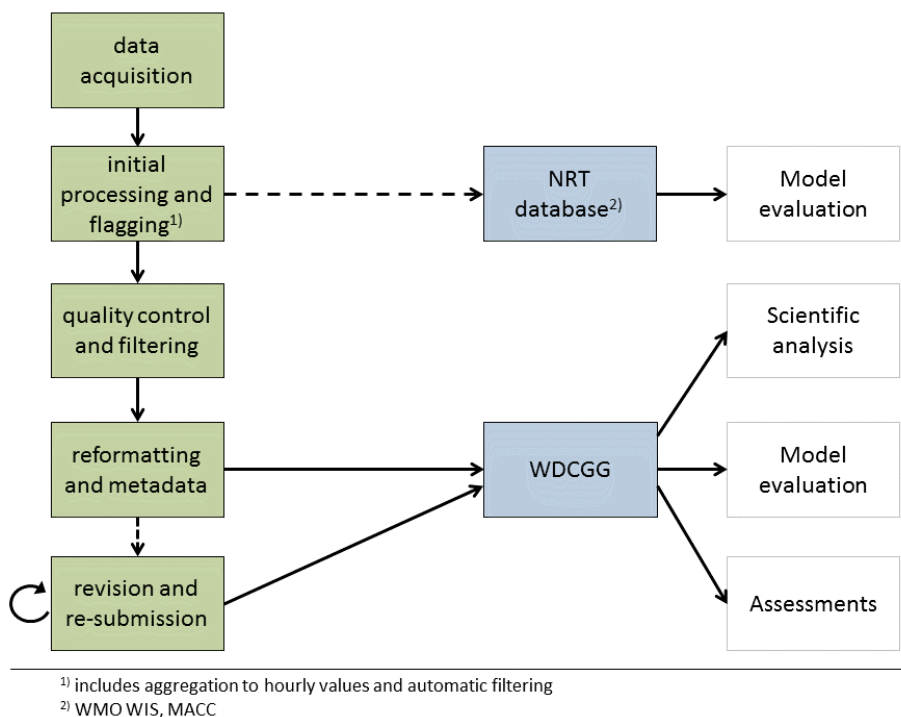


Figure 8 - Outline of the main elements of data processing and data management for GAW ozone station data. Green boxes denote processing steps that take place at the measurement station or at the institution which oversees the station operation

10.2 Summary of best practices for data processing and data management

As discussed in Section 8, the observations at the station are recorded as a raw data record that consists of valid ambient observations, instrument checks (zeros, spans, calibrations) and periods of instrument malfunctioning, technical tests, or other conditions leading to “invalid” data. These data are reviewed, flagged and processed to produce ambient ozone mole fractions as part of the station record of observations.

There are several guidelines that are proposed to assist this process. These are taken from GAW documents (*WMO, 2003; WMO, 2009b; WMO, 2009c*), augmented by additional information from, and practical experience of, members of the GAW Reactive Gases SAG and the World Data Centre expert team (ET-WDC). The GAW Guidelines for Data Management (*WMO, 2003*) specify that the organisation producing data is responsible for design and maintenance of an appropriate data archive. It is recognized that different laboratories may choose to implement the guidelines and examples in different ways.

- Given modern computing memory capacity, the raw data of 1 minute resolution, should be stored along with the processed data that are archived at the station
- A standardised data flagging system should be used (see Section 10.3)
- All raw data must be kept in electronic form in at least two physically different and safe locations and must not be altered in any way
- Provisions must be in place to guarantee readability of the raw data files for the indefinite future. This may require reformatting the raw data which is not considered an alteration
- Raw data and the relevant logbook(s) must be readily available
- In order to facilitate the analysis of the station data record, time averages of 1-hour, 1-day, 1-month, and 1-year should be generated
- Data products (such as aggregates) should be calculated from the highest frequency data available. All procedures must be unambiguously documented
- Where applicable, on each aggregation level two separate data sets should be produced for “all valid data” and “valid background data”, respectively (see Section 10.5)
- The meteorological variables: temperature, pressure, relative humidity, wind direction and wind speed should be archived along with the ozone data
- The processing algorithms, all relevant constants and coefficients, the date and time of processing, the names of the responsible persons, and affiliation should be stored in the header of each data file
- The version of the dataset should be clearly marked in standardized metadata attributes, and all changes that are applied to a dataset as a result of a revision process shall be described
- Data and corresponding metadata should be recorded and archived either with reference to Universal Time Coordinate (UTC) or a time scale with clearly indicated relationship to UTC
- Date/time stamps should be expressed in ISO standard format⁷
- Date/time stamps (*WMO, 2009b*) must clearly indicate that they mark the beginning of the sampling period covered for continuous measurements⁸, and the start time and end time of sampling for discrete measurements⁹.

⁷ The ISO 8601 notation for date and time is yyyy-mm-dd HH:MM:SS or: yyyyymmddHHMMSS. This notation does neither specify the time zone nor any deviation from it (such as day light savings time). This information must be given in the context. If the date and time refer to Universal Time Coordinated (UTC) and this is not obvious from the context, a ‘Z’ may be added to the date and time string.

⁸ Measurements are called ‘continuous’ if air is continuously sampled and the analytical result is an integral with a specified temporal resolution. These analyses are usually averaged internally by the instrument to obtain aggregates. A typical example is an UV analyser: air is passed continuously through the sample cell, readings are taken every few seconds and aggregates of 1 minute or more are reported.

⁹ Measurements are called “discrete” if air is sampled and analyzed at discrete points in time. Tropospheric ozone measurements by lidar may fit into this category.

10.3 Initial (automated) validation of the data

There are a number of criteria that can be applied to the data automatically to check the quality of the data. They are presented below with examples of the check values that are applied at Cape Grim GAW station. Automatic software procedures can be set up to run along with the data processing to alert the operator if:

- Ambient ozone mole fractions (1 minute) are below/above extreme values, e.g. less than or equal to 0 nmol mol^{-1} ¹⁰, $> \text{MAX}$ ¹¹ (MAX = $100 \text{ nmol mol}^{-1}$ at Cape Grim, could be larger at other stations, but never $> 300 \text{ ppb}$ in the troposphere)
- The change in ambient ozone mole fractions (1 minute) between two successive minutes exceeds MAX in either direction (e.g., MAX = 5 nmol mol^{-1} at Cape Grim)
- The difference between ambient ozone mole fractions measured by two instruments (1 minute) in the same minute exceeds 5 nmol mol^{-1} in either direction (this threshold value should be applicable at all stations running two instruments in parallel)
- Ambient hourly standard deviation of 1-minute ozone mole fraction is extreme, either $< \text{MIN}$, or $> \text{MAX}$ (MIN = $0.1 \text{ nmol mol}^{-1}$ and MAX = 5 nmol mol^{-1} at Cape Grim, both threshold values may be larger at other stations)
- Change in zero value between two successive zero measurement periods is large, e.g. $> \text{MAX}$ (e.g., MAX = 1 nmol mol^{-1} at Cape Grim for zero measurements on consecutive days)
- Change in span value between two successive span measurement periods (e.g. different days) is $> \text{MAX}$ (MAX = 3 nmol mol^{-1} at Cape Grim, depends on instrument, but should be similar for all stations).

These checks throw up data quality flags which must be manually inspected by the Responsible Investigator to either validate or invalidate the data. The Responsible Investigator should also confirm that all invalid data according to the station and instrument logs have been flagged as such.

It may be of use to run the above validation tests twice with two different threshold levels for each test. The first test could use less stringent criteria which would normally be exceeded only in the case of instrument malfunctioning or other problems at the station (for example values $< -10 \text{ nmol mol}^{-1}$ or $> 300 \text{ nmol mol}^{-1}$). In such events, the operator should be notified immediately so that technical checks can be performed and the problem can be fixed. The second validation with more stringent thresholds would be used to populate the data flags and thereby serves two main purposes:

- Provide the instrument RI with some indication of potential data problems for the subsequent validation and visual inspection of the data
- Filter potentially invalid data to increase likelihood that only valid data will be used in near-real-time applications if the data are transmitted in near-real-time.

These data flags feed into a systematic data flagging system described in the next section.

10.4 Data flagging

The purpose of data flagging is to obtain, at the end of the processing of the measurements, a time series of mole fractions that represents ambient conditions and to clearly identify artefacts as such. No entries should ever be removed from the original (raw) data set. Samples designated as not representing atmospheric composition should be identified by a character in the data string (flagged). The periods of automatic and/or manual calibration or maintenance as well as instrument problems should be clearly flagged. Instrumental problems are sometimes not obvious and identifying them in the time series may require significant experience.

¹⁰ Note that ozone values of 0 nmol mol^{-1} occur rarely in the background atmosphere, and in the urban atmosphere only in the presence of high NO concentrations. Values $< 0 \text{ nmol mol}^{-1}$ can occur in the event of an instrument zero drift. In either event the instrument RI needs to investigate and, where possible, determine the cause of the observations.

¹¹ MAX and MIN take on different values for this and subsequent data checks.

A well-maintained log of station activities, instrument behaviour and observations made by station staff is indispensable to aid this process.

One of the requirements regarding the observations within the GAW Programme is open data availability. Wider data utilization in the products and services is beneficial for the partners of the programme. In this respect, all observations need proper description to allow for proper interpretation. Standardized flagging of the data appears an essential element of the data description. The WDCGG in GAW Report No. 188 (*WMO, 2009b*) describes a system of flags based on a NOAA standard procedure first presented in WMO (2003). This system uses three characters for the flag represented here by ABC. The characters can be either a period or an alphanumeric character, e.g. "...” or “X.” or “.Y.”. The definitions of the columns given by NOAA are:

Column A REJECTION flag. An alphanumeric other than a period (.) in the FIRST column indicates a sample with obvious problems during collection or analysis. This measurement should not be interpreted.

Column B SELECTION flag. An alphanumeric other than a period (.) in the SECOND column indicates a sample that is likely valid but does not meet selection criteria determined by the goals of a particular investigation.

Column C INFORMATION flag. An alphanumeric other than a period (.) in the THIRD column provides additional information about the collection or analysis of the sample.

WARNING: A "P" in the 3rd column of the QC flag indicates the measurement result is preliminary and has not yet been carefully examined by the RI. The "P" flag is removed once the quality of the measurement has been determined.

The system is presented in Table 2 with examples of the flags that could be appropriate to the recording of tropospheric ozone data.

We recommend the adoption of such a three-category flagging for the ozone data with a fixed convention for the flags so that the data may be machine read and automatically incorporated into both modelling and analysis tools by any users globally.

Table 2 - Suggested flags for tropospheric ozone data based on the scheme originally suggested by WMO (2003)

Flag	Rejection (Measurement)	Selection (Environment)	Information (Operations)
X.P	initial unprocessed	no special conditions	unvalidated
..P	Processed, passed automatic tests	no special conditions	unvalidated
...	processed	no special conditions	validated
.N.	processed	non-background conditions (not specified)	validated
.B.	processed	biomass burning influence	validated
.R.	processed	urban plume	validated
C..	calibration, zero or span	n/a	validated
S..	special study, not to be included in the ambient measurements data set	n/a	validated
I..	invalid data, not for interpretation	n/a	n/a
I.I	bad data	n/a	Inlet failure
I.A	bad data	n/a	Analyser failure
I.P	bad data	n/a	Positive outlier value
I.N	bad data	n/a	Negative outlier value
I.R	bad data	n/a	Too rapid change in mole fraction values
I.C	bad data	n/a	Consistency problem between two analyzers
I.V	bad data	n/a	Extreme variability (lower or higher than normal)
I.Z	bad data	n/a	Drift in zero measurement

10.5 Near-real-time data delivery

Where possible, unvalidated raw data that have been converted to units of mole fraction and quality-controlled with automatic tools (e.g. testing for outliers, abnormal variability, etc.) should be made available for data assimilation purposes and validation of global and regional forecast services of atmospheric composition and air quality. The GAW NRT working group is establishing guidelines and procedures for this process which aim at minimizing the effort for the data providers while at the same time maximizing the usefulness of the data for the forecasting services (*WMO, 2010a*).

10.6 Data quality control and further processing

Recent data should be visually reviewed in regular intervals, either when on-site or by remote access or after transfer of the data to the main laboratory. The software should provide the capability to plot past and recent raw data (e.g. for simple visual inspection of the data). Some clues to the correct operation of the analyser can be obtained from the instrument values during span and zero checks and ambient readings. Training of station staff in these procedures is available through the GAWTEC training programme.

Additionally plotting the ozone mole fractions in conjunction with some other variables that are expected to correlate with surface ozone (i.e. CO, NO_y, or NO_x mole fraction, wind speed and direction, temperature) or influence the measurements (i.e. snow fall, freezing) is recommended. The purpose of this is to identify data points that are clearly outliers. More sophisticated data analysis, e.g. curve fitting to the annual cycle of surface ozone observations (*Weatherhead et al., 1998*), is also a useful tool for identifying outliers. Outliers should be flagged as such in the raw data (see above). Considering a measurement result to be a random variable, 'outliers' are confined to values that are not sampled from the same distribution as the regular measurements.

Examples include abnormal readings due to a power surge, defective sensors, contamination, or operator interference. Values that remain unexplained even after scrutiny and within a reasonable distance from the median should be regarded as 'extreme' values. Whereas 'outliers' can be removed from the analysis of a set of experimental results, 'extreme' values cannot. All data should remain in the data set, appropriately flagged.

The calibrated and validated ozone data of high temporal resolution is aggregated to hourly, daily, monthly and yearly averages. In each aggregation step, a >66% criterion for valid data shall be applied. If the station is frequently influenced by non-background air masses, two separate data sets should be compiled for each aggregation level: one that includes all valid data, and one that includes only the measurements under background conditions (see next sub-section).

10.7 Identification of hemispherically or regionally representative observations

Determining the spatial and temporal representativeness of data is essential to ensure they are used properly in scientific analysis. This representative data can be used in empirical analyses as well as when comparing observations with models.

This issue occurs when comparing observations with models, where "model-data mismatch" (errors introduced because the spatial and temporal resolution of the model is different from that of the data) must be assessed to properly estimate uncertainties in model processes and boundary conditions. One criterion that has been used to facilitate model-data comparisons is to select observational data that are representative of the global or regional background atmosphere. In this context, representative means uninfluenced by local sources and sinks that occur on a spatial scale either less than or much less than that of the model grid cell.

There are several ways how the representative background data are chosen. Examples of the selection criteria are listed below and then a discussion with references follows.

Selection criteria:

- Wind speed and direction
- Wind speed and direction and particle number concentration
- Radon concentration
- Air trajectories from numerical weather prediction
- Mole fractions of other trace species, notably CO
- Tracer/tracer mole fraction ratios, such as NO_y/CO
- Criteria based on statistical time series analyses.

The selection of data by wind speed and direction is a valuable initial tool for excluding local and distant influences on ozone production and destruction at a background site. The sites have to be chosen so that it has at least one wind sector where the air parcels have no major exposure to ozone sources upwind, and this is the background sector. Almost all background sites satisfy the criteria of availability of the background wind sector. Nevertheless, the presence of local circulations (e.g. breeze or up-slope) can impact this "background wind sector". Therefore multiple criteria may be needed to select data free from local influences. The distribution of time for which background air can be sampled may have a strong seasonal variability.

Several other techniques are appropriate to filter the observations for background conditions. One involves the use of calculated air back trajectories usually obtained from a numerical weather prediction model. These trajectory calculations often follow a cluster of particles backwards in time and indicate any possible contact of the cluster of particles (or air parcel) with regions where ozone sources and sinks are active (*Cui et al., 2011*).

The other method involves the use of chemical tracers in the air which indicate either exposure to pollutant sources (particles, CO and either NO_x or NO_y) or exposure of the air to land surfaces (radon). Fine particles (condensation nuclei) are produced in towns and mark urban plumes for long distances downwind (*Ayers et al., 1982*). Similar effects occur from vegetation

fires. Larger particles such as soil dust and sea salt are less useful as air mass markers. Both CO and NO_x can be markers of combustion, both fossil fuel and biomass burning, and either individually or in ratio they are recognised tracers for polluted air (*Trainer et al., 1993; Zellweger et al., 2003; Zanis et al., 2007*). Radon is emitted from land surfaces and has a half-life of 3.8 days and as such its atmospheric concentration is an excellent indicator of recent contact with land surfaces (*Gras and Whittlestone, 1992; Zahorowski et al., 2004, 2005; Crawford et al., 2007*). In mountainous terrain, the specific humidity of the air mass may be an effective tracer of previous history (*Henne et al., 2005*).

Statistical filtering of the data can also be applied to select background conditions, based on the assumption that the background representative concentrations lie towards the centre of a frequency distribution and can be extracted by statistical means. Identifying the optimal filter criteria for each site is in many cases subject of ongoing research. If such filtering is applied to the validated data set (i.e. in the aggregated hourly, daily, weekly, monthly, annual mean files), the filter criteria should be listed in the accompanying metadata, and the station description (on GAWSIS) should include a detailed description of the filtering procedures.

10.8 Data submission

The global data archive for tropospheric ozone (in situ continuous) measurements is the World Data Centre for Greenhouse Gases (WDCGG) maintained by the Japan Meteorological Agency (<http://ds.data.jma.go.jp/gmd/wdogg/>). The WDCGG has published a data submission and dissemination guide (*WMO, 2009b*) that explains the requirements and procedures to be followed. All validated tropospheric O₃ data obtained as part of the GAW Programme should be submitted within one year to the WDCGG. Continuous and quasi-continuous data may be reported as hourly averages (preferred) or higher aggregates. The data must be accompanied by appropriate metadata (see Section 10.10) and these Measurement Guidelines recommend that the data should contain the data quality flags defined in Section 10.3. WDCGG also accepts campaign data. Submission of ancillary data (i.e. meteorological parameters) is strongly encouraged. Data submitters should consult the WDCGG data submission guidelines (*WMO, 2009b*) or contact the WDCGG for instructions.

The requirements for submission include the availability of information about the station, information about the measurement programme, and the observational data in the format specified in Annex 2 of the WMO (2009b) report.

10.9 Data revision

Under certain circumstances it may be necessary to replace an existing archived data record in the WDCGG by an updated one. This may occur if changes in the calibration (for example after a re-calibration to the primary standard or after an audit procedure) are identified, if new procedures for the data quality control are implemented and the old record is being reprocessed, etc. One specific example is discussed in Section 4.1. As explained there it is possible that the value ascribed to the ozone absorption cross-section may be revised in future. For this reason it is desirable to identify a particular tropospheric ozone scale in metadata. For example, it is suggested that the current scale be explicitly named, e.g. the Hearn O₃ X1961 Scale. A subsequent scale would be differently named. The scale is specified under the heading "Current Scale" in the section "Processing/Calibration" of metadata in the record at the WDCGG. This explicit recording of scale will be essential for systematic data analysis if a change is made to the ozone absorption coefficient.

If a revised data set is submitted to the WDCGG the data provider should ensure that it carries an updated version number and that all changes to the data are clearly documented in the metadata, including the person who did the changes and the date when the changes were made.

10.10 Metadata

Metadata is structured information that describes, explains, locates, or otherwise makes it easier to retrieve, use, or manage an information resource. Metadata is often called data about data or information about information (*NISO, 2004*). Systematic approaches to recording metadata

of scientific data sets have existed for several decades such as the Directory Interchange Format (DIF, 2012).

There is a growing demand for comprehensive metadata to better utilize measurement data. As well as giving station site information and supporting the administration of the data in the WDCGG, the metadata are required so that:

- The data sets can be located through interoperable web catalogues and data access services
- The quality of the data can be determined from the metadata information
- The data can be utilized by any interested party.

WDCGG as the designated global archive for tropospheric ozone data, published a data submission and dissemination guide as the GAW Report No. 188 (WMO, 2009b). Annex 5 of the document provides a comprehensive description of what information should be gathered in metadata at the WDCGG. Reacting to ongoing developments with respect to the WMO Information System (WIS) and standardisation of geospatial information, the current metadata guidelines will undergo revision over the coming years.

To ensure the possibility of retrospective and comparative analyses, the following information should be included in the metadata of each data file:

- The instrument and supporting system being used and their characteristics and performance
- Traceability of the instrument to the primary standard.

Much of this information is covered in the headings supplied by the WDCGG for metadata. However the data submitted by stations are not always comprehensive. An examination of the WDCGG metadata headings indicates that the combined standard uncertainty of the tropospheric ozone measurement is not currently explicitly covered. An additional heading of "combined standard uncertainty" would be useful for evaluating instrument performance. Other information such as the condensed results of instrument comparisons, when two analysers are run simultaneously at the station, would be useful for both current and future evaluation of instrument performance.

WMO enhanced the metadata exchange function within and beyond the various WMO programmes in the framework of the WIS (WMO Information System) Project (http://www.wmo.int/pages/prog/www/WIS/index_en.html). In the WIS framework, the WDCGG was designated as one of the Data Collection or Production Centres (DCPCs) in 2011 and all the metadata archived in the WDCGG are made available from Global Information System Centres (GISCs) with their Discovery, Access and Retrieval (DAR) function. As of April 2012, WDCGG metadata are searchable from two GISC portals (<http://gisc.dwd.de/>, <http://www.wis-jma.go.jp>).

A key factor (raised in Section 2) is that the metadata should explicitly state whether the ozone mole fraction is measured relative to dry air or moist air.

A. DISTRIBUTION AND TRENDS OF TROPOSPHERIC OZONE

A.1 Global tropospheric ozone budget

There are four key processes that regulate tropospheric ozone. These are production of ozone through chemical reactions in the air, intrusions of ozone via stratospheric-tropospheric exchange (STE), chemical destruction of ozone in the air and destruction of ozone via deposition at the earth's surface. These four processes are shown in the schematic in Figure 9.

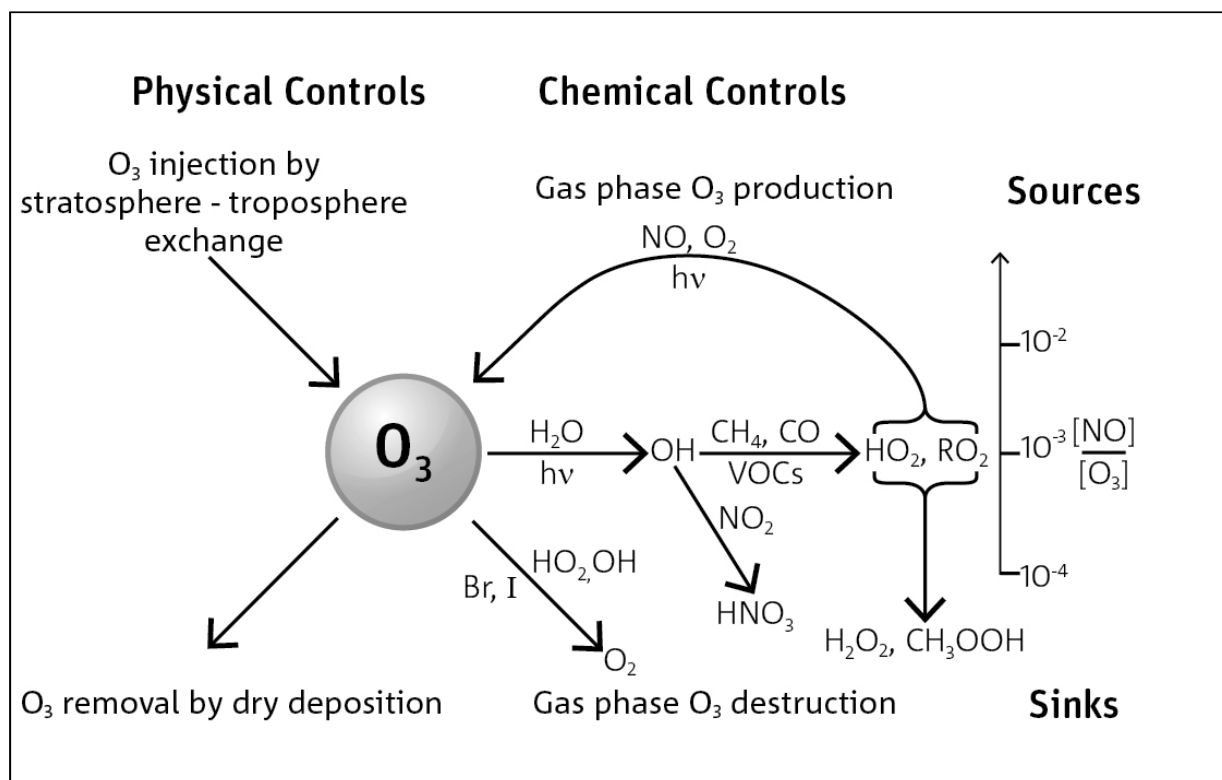


Figure 9 - The physical and chemical processes controlling tropospheric ozone. Processes indicated in the top half of the figure are sources and processes; in the bottom half of the figure are the sinks for tropospheric ozone. The key sinks for the short lived radicals produced from tropospheric ozone are also indicated. Nitric oxide titration of ozone near major NO sources is omitted as the figure represents the troposphere away from the immediate vicinity of major sources.

(Figure courtesy of Ian Galbally, CSIRO Marine and Atmospheric Research)

The combination of atmospheric transport and these processes leads to the observed distribution of ozone in the troposphere. Table 3 presents the budget of tropospheric ozone as determined from a study of 26 models by *Stevenson et al. (2006)*. Ozone has a lifetime of 22 days in the troposphere; hence the long-term ozone trend arises from very small changes in the sum of these terms. Each of the terms has a strong seasonal cycle which drives the seasonal cycle of tropospheric ozone concentration.

A.1.1 Stratosphere – troposphere exchange

Tropospheric ozone is influenced by transport of ozone-rich air from the stratosphere into the troposphere which happens primarily in the mid-latitudes during winter/spring. This exchange is accompanied by the return of ozone-depleted air from the troposphere into the stratosphere that occurs primarily in tropical regions. This ozone of stratospheric origin is dispersed throughout the troposphere and generally contributes only to a small fraction to the ozone present in surface air, although there is some debate in the literature about the actual magnitude of this influence. *Flocke*

(1992) made an extrapolation out of an ozone / alkyl nitrate correlation, leading to a “non-photochemical produced” ozone mixing ratio of 18 ± 9 ppb¹². Pre-industrial ozone measurements gave readings around 10 ± 5 ppb (Volz and Kley, 1988).

Table 3 - The global budget, atmospheric burden and lifetime of tropospheric ozone (Stevenson et al. 2006)

Process	Source (Tg y ⁻¹)	Sink (Tg y ⁻¹)
Stratosphere-troposphere exchange	552 ± 168	
Gas phase chemical production	5110 ± 606	
Gas phase chemical loss		4668 ± 727
Dry deposition		1003 ± 200
<hr/>		
Burden (Tg O ₃)	344 ± 39	
Lifetime (days)	22.3 ± 2.0	

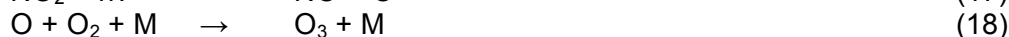
A.1.2 Chemical processes

Gas phase chemical processes that may perturb the concentrations of background tropospheric ozone involve both sources and sinks (Seinfeld and Pandis, 2006). The two sets of precursors necessary for ozone production, along with sunlight, are (a) nitrogen oxides and (b) VOCs, CO and CH₄. For descriptions of the sources of these compounds the reader is referred to either Seinfeld and Pandis (2006), Brasseur et al. (2003) or the GAW Reports No 171,185, 192 and 195 (WMO, 2007a; 2009a; 2010b; 2011a).

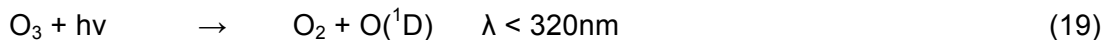
The most rapid process to affect tropospheric ozone is its reaction with nitric oxide.



This means that near a NO source, ozone will be titrated out of the air. However, in the presence of sunlight an equilibrium between ozone production and loss via NO and NO₂ is established within minutes, as shown in equations 16 to 18. This equilibrium is known as the photo-stationary state or Leighton relationship.



Ozone’s key role in tropospheric chemistry, through the formation of the OH radical, is initiated by the photolysis of ozone to form atomic oxygen in the singlet excited state. This excited atomic oxygen can react with water vapour forming the reactive hydroxyl radical.

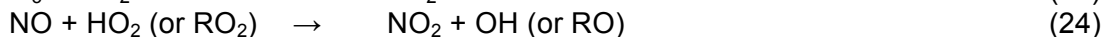


Hydroxyl radicals react with CO, CH₄, volatile organic compounds (VOCs), dimethyl sulfide, SO₂, etc. initiating the oxidation of these compounds in the troposphere. In this process RO₂ and HO₂ radicals are formed via equations 21 and 22.



¹² The issue of ozone units is discussed in Section 3.1. The units nmol mol⁻¹ and ppb are used interchangeably in this document with ppb reflecting historical analyses and nmol mol⁻¹ reflecting the unit of choice of current and future analyses.

RO₂ and HO₂ radicals can either destroy ozone via equation 23 or produce ozone via equation 24 (followed by equations 17 and 18), depending on the abundance of NO. In a modelling study Crutzen (1979) calculated that in the remote troposphere the NO/O₃ ratio must be greater 2.5·10⁻⁴ for net ozone production to occur, otherwise there will be net destruction. Observations at Cape Grim in summer gave this ratio as 1·10⁻³ (Galbally *et al.*, 2000).



There are many other reactions regulating the concentrations of OH, HO₂, and RO₂ radicals, and thus indirectly the ozone production and loss rates. In the upper troposphere photolytic destruction of acetone represents an important OH source. Ozone also reacts with unsaturated hydrocarbon compounds (notably biogenic species), a process that can noticeably influence ozone concentrations in (tropical) forest regions and at night. These chemical transformations are also the basis of ozone production in urban photochemical smog, biomass burning plumes, and the background troposphere. In polar regions and in the marine boundary layer, ozone reactions with halogen-containing compounds can have a major role in photochemical ozone destruction (Barrie *et al.*, 1988; Simpson *et al.*, 2007).

Precursor emissions can affect ozone differently in the individual seasons. A NO increase is expected (1) to decrease ozone in the immediate vicinity due to the effect of ozone titration by NO, and subsequently to either (2) increase ozone by photochemical formation downwind of emission sources in the well sunlit warm season or (3) decrease ozone in winter downwind due to the effect of ozone titration by NO and the limited light etc.

A.1.3 Dry deposition of ozone

The physical loss mechanism of tropospheric ozone is ozone destruction at the underlying surface, commonly called dry deposition. Ozone within air is destroyed when it comes in contact with soil and plant surfaces or with highly reactive gases released from the soil and plants. This destruction by soil and plants is sufficiently rapid so that in light wind conditions overnight in mid-continental areas, ozone can be depleted for heights up to 100 m (Galbally 1968). At water, snow and ice surfaces ozone destruction is much slower (Galbally and Roy, 1980; Helmig *et al.* 2007, 2012) and ozone depletion due to surface destruction is not readily observed. Consequently only very small diurnal changes in ozone concentration are observed from ships and at coastal and island sites when sampling in on-shore winds and in ice and snow covered environments (Oltmans, 1981; Ayers *et al.*, 1992; Helmig *et al.*, 2007).

A.2 Spatial distribution

Locally, at a measurement site, ozone concentrations are influenced primarily by advection of ozone from other regions and from above (at mountain sites also from below), fast chemical production and losses (e.g. titration with NO), and dry deposition occurring in the region around the station. Tropospheric and surface ozone observations from different parts of the world will have different regional meteorological influences. The larger scale meteorology varies from monsoons and dry seasons, trade winds and the doldrums in the tropics, the continual migration of cyclones and anti-cyclones in the mid-latitudes and the tendency to seasonally steady winds in high latitudes. On the local meteorological scale there are land/sea breezes, upslope/downslope winds and other orographic effects. These meteorological processes have a significant influence on the observed ozone concentrations.

The available observations show that tropospheric ozone is highly variable both in space and time, on long and short scales as foreshadowed above. The following describes the broad-scale features. Over the remote oceans, observations show low ozone amounts within the tropical Hadley circulation with little or no vertical gradient in mole fraction, then higher concentrations at mid latitudes, with an increase with height, corresponding to the additional source of tropospheric ozone from STE as well as in-situ chemistry. Over the continents and nearby oceans in the lower troposphere different behaviour is observed. In July, northern summer, major regions of elevated lower troposphere ozone are observed over USA, Europe and east Asia from urban/industrial

activities, and regions of elevated ozone over the tropics due to both biomass burning and other human activities (Figure 10). Satellite observations of tropospheric ozone have revealed much detail about the spatial distribution including the discovery of the regional tropospheric ozone maxima off southwest Africa over the Atlantic Ocean (*Fishman et al., 1991*).

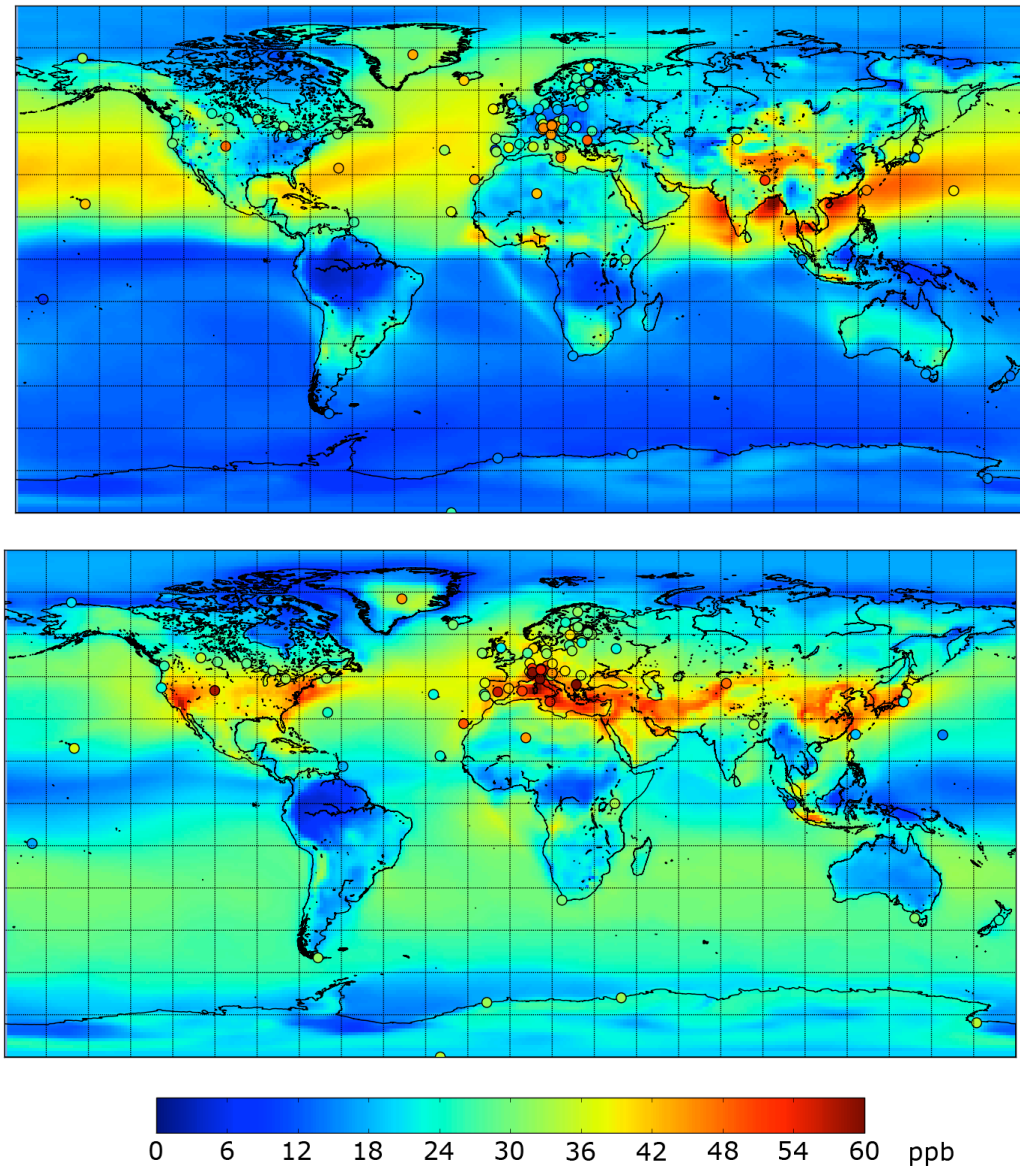


Figure 10 - Global distribution of near surface ozone mole fractions measured by the GAW network stations superimposed on model simulated mole fraction fields from the MACC (Monitoring Atmospheric Composition and Climate) reanalysis. GAW measurements were averaged over the period 2000 to 2009, the MACC reanalysis spans the period 2003 to 2010. Top: monthly mean for January, bottom: monthly mean for July. (Figure courtesy of Martin Schultz, Forschungszentrum Jülich, Germany)

A.3 Temporal changes in tropospheric ozone

A major objective of the GAW Programme is to determine long-term changes in tropospheric ozone. The earliest observations that can be compared on the current ozone scale are from the observatory at Montsouris in Paris, made between 1876 and 1910 (*Volz and Kley, 1988*). These observations from the 19th century provide the benchmark against which it can be established that surface ozone concentrations have approximately doubled in the last 150 years, certainly in Europe. Surface ozone concentrations at unpolluted sites in Europe increased by more

than a factor of two between the 1950s and the early 1990s (*Stahelin et al., 1994*). More recently there have been substantial increases in tropospheric ozone since the 1960s at many background sites, although during the last decade these increases have either ceased or reversed at some sites (*Oltmans et al., 1998, 2006; WMO 2011c; Logan et al., 2012; Parrish et al., 2012*). The relationship of these long-term tropospheric ozone trends to trends in precursor emissions is an area of active scientific work that will not be addressed here.

Besides the long-term changes it is also of interest to investigate other modes of variability, such as interannual variations or changes in the seasonal cycle. As an example, one large-scale tropospheric ozone phenomenon recently discovered is that the tropospheric ozone column amount over the Indonesian archipelago oscillates in unison with ENSO (*Ziemke et al., 2010*).

B. SELECTING TROPOSPHERIC OZONE MONITORING SITES IN BACKGROUND ENVIRONMENTS

B.1 Considerations for expanding the global network of tropospheric ozone measurements

To quantify the distribution and trends in tropospheric ozone, and to understand the processes regulating tropospheric ozone, there is a need of an observational base of ozone measurements in the troposphere that covers the different physical/chemical regions of the atmosphere. Because of the short global average lifetime of ozone in the troposphere of approximately 22 days (*Stevenson et al., 2006*), ozone is not well mixed in the troposphere, and ozone concentrations in the two hemispheres are essentially decoupled. Understanding and quantifying the processes that effect tropospheric ozone requires observations of ozone concentrations and associated physical and chemical phenomena throughout the troposphere, including (1) the free troposphere; (2) the remote marine boundary layer; (3) the remote continental boundary layer, and (4) the parts of the marine and continental boundary layer affected by intense anthropogenic and/or natural pollution sources (e.g. urban/industrial complexes, regions of extensive biomass burning). GAW observations are normally associated with categories 1, 2 and 3 above and perhaps in the case of intense biomass burning, category 4. In the following subsections, the characteristics associated with ozone observations in these environments are discussed.

When either cities, with residential combustion and motor vehicle emissions, or industrial complexes with combustion of fossil fuels or biomass burning occur upwind of a station, they can cause perturbation to the ozone in air masses originating from the background atmosphere, and hence diminish the usefulness of sampling for background ozone at that location. Observations affected by intense anthropogenic activities associated with precursor sources (e.g. urban/industrial complexes) are within the domain of regional air quality. A brief outline of the conditions appropriate to various monitoring regimes and the associated variables are given in Table 4. Due to the fact that tropospheric ozone is not directly emitted and influenced by several factors, characterisation of the chemical environment of a measurement site is best performed by observing ozone precursor concentrations (i.e. primary pollutants). Table 4 provides a classification of environmental conditions based on NO_x mole fractions, as these species are most closely linked to the fast ozone chemistry (see Section A.2). Similar classifications, albeit less robust, can be derived from observations of CO, VOC, or particulate matter.

Table 4 - Indicative measures of atmospheric conditions for ozone measurements in different environments

Region	Ozone variability*	NO _x mole fraction	Footprint	Ozone/NO titration events
Global background	0.5 ppb	Median < 100 ppt	~ 500 km	Never
Regional continental boundary layer	< 2 ppb	Median < 1 ppb	~ 100 km	Rare
Urban/Industrial background	> 2 ppb	Median < 5 ppb	~ 10 km	Occasional
Urban	> 2 ppb	Median > 5 ppb	< 10 km	Daily

*average standard deviation of minutely values making up an hourly mean

The choice of location for a GAW observing station is a decision of major importance. Considering that these stations are intended to operate for longer periods, the benefits of a good choice are enormous. The location both affects the effectiveness of the monitoring and the ease or cost of the monitoring. The first factor in choosing a location of a background monitoring station is to ensure that it can adequately sample the atmosphere unaffected by intense anthropogenic or natural sources. This will be discussed in the following sub-sections. The second factor in choosing a location is to ensure the ease of maintaining the monitoring programme that could run for a 30 to 50 year period. The evaluation of any location as a site for a GAW station must include consideration of the local and regional meteorology and the influences these have on bringing either polluted or background air to the sampling location. The characteristics of sites in various locations are discussed in the following sections.

B.2 Characteristics of surface ozone measurements in different environments

Surface ozone measurements within different environments in the atmosphere show different behaviours. In Figure 11 and in the following sub-sections, these behaviours are explored. This is done specifically to assist those newly introduced to tropospheric ozone studies to appreciate what may be expected of ozone observations in these different environments.

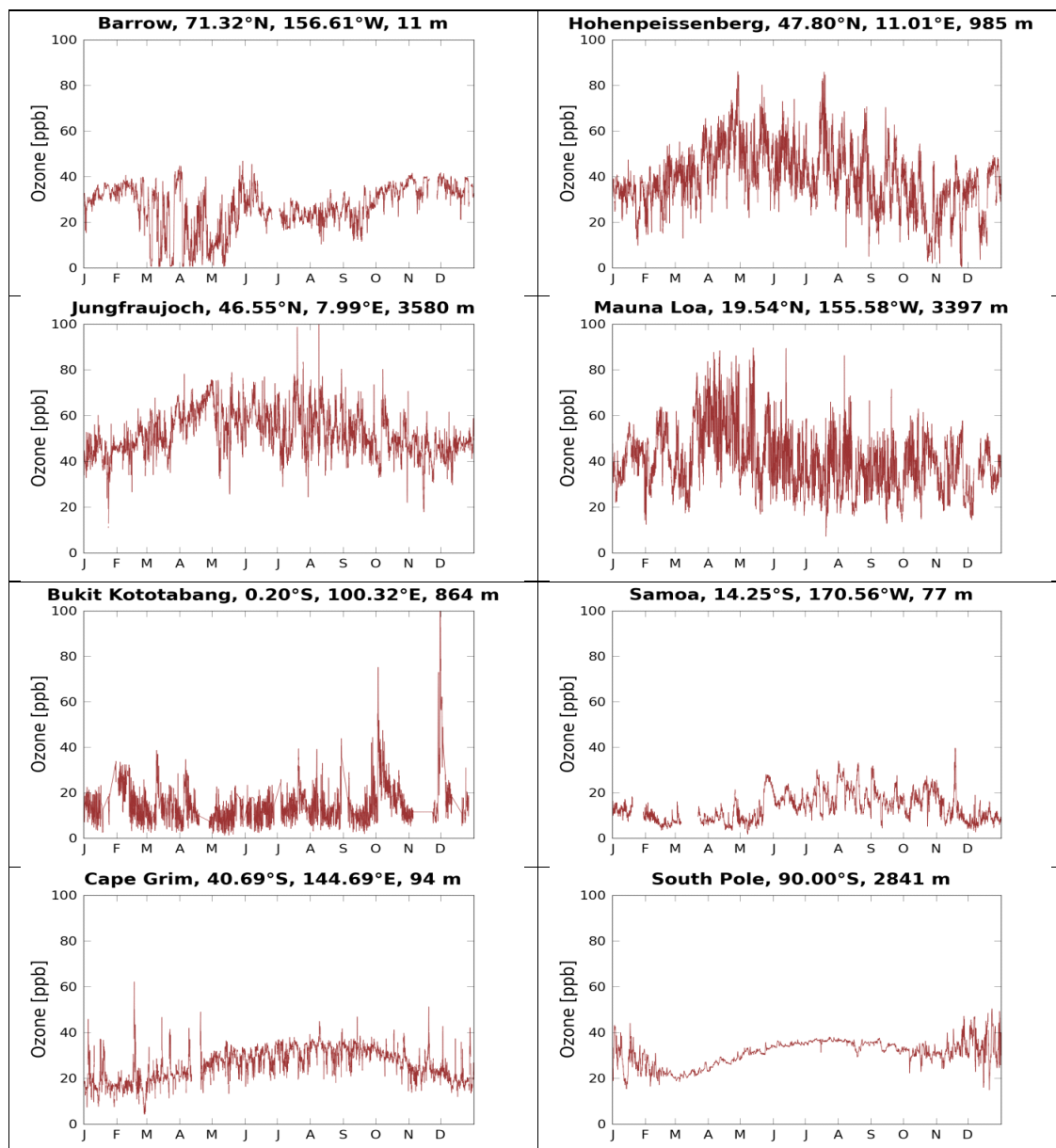


Figure 11 - Surface ozone mole fractions for hourly data from selected GAW stations for 2007, except Samoa, which is presented for 2006. Data are retrieved from the WDCGG

B.2.1 Tropical coastal and island sites

A coastal or island site in the tropics will experience steady trade winds for much or all of the year in which case wind directions may remain relatively constant for months on end, perhaps a monsoon season and perhaps occasional tropical cyclones. Local circulations such as land/sea breezes may be strong. Generally ozone is in lower concentrations in the tropical marine boundary layer because of its loss by photolysis and OH production. The seasonal variation may be affected by the occurrence of monsoons and trade wind circulations. The diurnal variation in ozone will generally show a minimum during the daytime. Occasional air transport events from the mid-latitudes will bring in higher ozone concentrations. The site at Samoa is an example of such location, and one year of observations is shown in Figure 11. The mole fractions are low, typically 5 – 20 ppb, and the annual maximum occurs in June to September, southern winter, a characteristic of ozone in the southern hemisphere troposphere.

B.2.2 Temperate coastal and island sites

Temperate coastal and island sites will be influenced by the passage of cyclonic and anti-cyclonic synoptic disturbances. Typically in the course of a week a wide range of wind directions will be experienced. As such, attention must be paid to identifying what is non-background air and background air. At a mid-latitude station such as Cape Grim (41 °S) shown in Figure 11, background air is sampled 25 to 55% of the time on a monthly average basis. The frequency of background and non-background conditions is driven by passing synoptic disturbances. The maximum ozone concentrations at Cape Grim occur in July to October, southern winter/spring, a characteristic of ozone in the southern hemisphere troposphere. In background conditions, the diurnal variation in ozone will generally show a minimum during the daytime. In some locations ozone concentrations may be influenced by upwind emissions from ship traffic, even over long distances (*Williams et al., 2010*).

B.2.3 High-latitude sites

GAW sites at high latitudes may be influenced by the near continuous presence of snow or ice cover, and two examples, Barrow (72 °N) and South Pole are shown in Figure 11. Because of the low ozone reactivity with water, snow or ice (*Galbally and Roy, 1980*) ozone loss on the underlying surface is not a major concern. Polar sites may have wind directions that remain relatively constant for months. Coastal sites may have ozone depletion events, which are related to halogen chemistry (*Barrie et al., 1988; Simpson et al. 2007*), and this is evident at Barrow during northern spring, March to May (*Oltmans, 1981; Oltmans et al. 2012*). The high reflectivity of snow and ice influences the photochemical reaction rates, because more UV radiation is available than what would be expected for these latitudes if one assumes a global average value for the surface UV albedo. In stable conditions with bright sunlight, local photochemical production has been observed due to NO_x emission from the snow (*Helmig et al., 2008a, 2008b*) and this is evident at the South Pole during November to February, centred on southern summer. The ozone concentrations in background air at the South Pole peak in winter/spring and fall to a minimum in summer/autumn as with other southern hemisphere sites. The seasonal variation at Barrow is more complex. With Polar sites, the location of the sampling relative to a nearby base camp may be a critical issue.

B.2.4 Mountain tops

A site located on a mountain top, where the mountain is at least 1 to 2 km above the surrounding land level, will generally be exposed to air from within the free troposphere. Two such sites, Jungfrauoch and Mauna Loa are shown in Figure 11. At these sites it is possible to identify, on occasion, air that has recently passed from the stratosphere to the troposphere (*Stohl et al., 2000*). This is generally not possible to do at sea level sites. The ozone concentrations at these northern hemisphere sites peak in April and May, northern late spring and early summer and fall to a minimum in December and January, northern winter. At mountain sites there can be, particularly in summer, a pattern of upslope winds during the daytime and downslope winds at night (*Kleissl et al., 2007*). Generally the downslope winds contain background air that is characteristic of the mountain top altitude. For the analysis of ozone data sets from mountain stations one should keep in mind that tropospheric ozone generally increases with altitude and the complexities of lower tropospheric vertical exchange of air needs to be considered (*Chevallier et al., 2007*).

B.2.5 Tropical continental boundary layer

Bukit Koto Tobang is presented as an example of a tropical continental site in Figure 11. Sampling sites in the tropical background continental boundary layer will experience low ozone concentrations in background air typical of the tropics. Regional sources of ozone due to precursor emissions from such activities as biomass burning, land clearing, agriculture and human settlements will cause occasional elevated ozone concentrations as seen in Figure 11. The seasonal ozone variation may be affected by these activities which can be influenced by seasonal meteorological conditions such as the occurrence of a wet/dry seasons. Under stable conditions, ozone depletion due to ozone deposition and NO titration will occur. The diurnal variation of ozone will generally be characterized by lower concentrations at night and higher concentrations during the daytime. Vegetation cover plays an important role together with local meteorology in (natural) trace gas emissions. For example, tropical rain forests are among the greatest emitters of isoprene, a reactive hydrocarbon species which is involved in the photo-chemical cycle of tropospheric ozone.

B.2.6 Temperate continental boundary layer

Temperate continental sites will experience similar meteorological impact to temperate island sites. Lower mountain top sites sample regional background ozone, and an example in Figure 11 is Hohenpeissenberg. Regional sources of ozone due to precursor emissions from urban centres, industrial complexes, biomass burning and agriculture may cause elevated ozone concentrations. Under stable conditions and close to pollution sources, ozone depletion due to ozone deposition and NO titration will occur. The diurnal variation of ozone will generally be characterized by lower concentrations at night and higher concentrations during the daytime. The seasonal variation in ozone concentration will be determined by the relative influences of regional sources of ozone and the ozone concentration in the background air. At Hohenpeissenberg the seasonal maximum is mainly in northern summer, May to July, with the minimum in late autumn - early winter. This seasonal variation is similar to that observed at higher-altitude sites in the northern hemisphere.

B.2.7 Tall towers

Tall towers (100-500 m) have not traditionally been used for sampling ozone in the background atmosphere. Tall towers have been proven very useful for sampling the long-lived greenhouse gases (<http://www.esrl.noaa.gov/gmd/ccgg/towers/>). The advantage of tall towers for ozone measurement is that they move the sampling away from the influence of ozone loss due to deposition at the earth's surface and from the immediate influence of nearby pollution sources. Micrometeorological theory would suggest that the footprint seen by a tall tower is tens to hundreds of km² and hence measurements made on them are more regionally representative than those made at the surface. GAW stations with extended programmes are encouraged to explore the use of tall towers for sampling the regional atmosphere. Normally the ozone analyser would be placed on top of a tall tower as the use of a long inlet system and the ozone analyser on the ground may lead to large ozone losses in the inlet.

C. REVIEW OF MEASUREMENT TECHNIQUES FOR OZONE IN THE TROPOSPHERE

A number of techniques are used (or have been used) for measurements of ozone in the background atmosphere. These include:

- Integrating techniques
- UV absorption techniques
- Chemiluminescence techniques
- Electrochemical techniques
- Cavity ring-down spectroscopy with NO titration
- Differential Optical Absorption Spectroscopy
- Multi-Axis Differential Optical Absorption Spectroscopy
- Tropospheric ozone lidar

A review is presented of each of these techniques along with information pertinent to their applicability to use in the GAW stations. Note that only the first five of these techniques (i.e. in-situ) can be traceable via a chain of calibrations to the primary standard as recommended by GAW. Remote sensing techniques (the last 3 methods in this review) would require a similar traceability chain which is theoretically possible via the knowledge of the ozone cross-sections at the particular wavelengths used in the instruments. This issue is currently under consideration by the ACSO committee (Absorption Cross-Section for Ozone).

C.1 Integrating techniques

Integrating techniques, especially the passive ones, belong to the "old-fashioned" measurement methods. For example, Christian Friedrich Schoenbein used dried paper, after being impregnated with a starched solution of potassium iodide. The paper strips were exposed for 8 - 12 hours to outside air under conditions that they were protected from direct sun and rain. The analysis for ozone was done by moistening the exposed strips with distilled water and measuring the degree of coloration of the blue iodine/starch-complex that develops by comparison with a chromatic scale usually graded from 0 to 10. Up to now a similar passive sampling method is used, whereby filter paper is impregnated with indigo, which is oxidised to the yellow dye "Isatin" by ozone (Cox *et al.*, 1999). These passive ozone measurements are simple, cheap and easy to handle, but need a long metering time period and have multiple possible interferences.

All active and integrating techniques use for ozone determination the oxidation of iodide to iodine followed by titration. Since this reaction is pH dependant, a neutral buffer is needed, otherwise the stoichiometry deviates from 1. Another problem of this method is the volatility of the formed iodine. This problem is solved by back-reducing the iodine to iodide by a compound which itself is oxidised in this process to a stable product. Examples of this are the reactions of thiosulfate to tetrathionate (Ehmer, 1959) or, in the "Montsouris" method, arsenite to arsenate (Volz and Kley, 1988). These techniques were used to make most of the higher-quality background ozone measurements available between the 1860s and 1980s.

Despite of their ease of operation and low set up and maintaining costs, these measurement techniques have substantial disadvantages. They are generally labour intensive, have multiple possible interferences and low time resolution. These techniques have mostly been replaced by more modern techniques and are not recommended for use for routine surface ozone measurements at GAW stations.

C.2 UV absorption techniques

The main principle of the UV method is based on the absorption of light in the UV region by the ozone molecule. The broad UV spectrum of ozone shows its maximum around 254 nm. This wavelength represents exactly the strongest emission line of an Hg lamp and the highest spectral

sensitivity of a UV detector, which is a caesium-telluride vacuum UV diode or UV-sensitive photomultiplier tube (PMT). The instrument measures the relative light attenuation between an air sample which remains unchanged (i.e. containing ozone) and one in which ozone has been removed. The ozone mole fraction is calculated via the Lambert-Beer law. Details of this measurement technique are given in Chapter 6.

Because of its high accuracy and precision, low detection limit, sufficient time resolution and ease of operation (almost no consumables), the UV absorption technique is recommended for use for routine surface ozone measurements at all GAW stations.

C.3 Chemiluminescence techniques

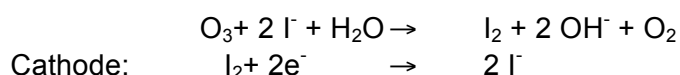
Chemiluminescence methods are typically based on the reaction of ozone with either reagent nitric oxide (NO) or reagent ethylene (C₂H₄). The former reaction generates NO₂ in an excited electronic state, and the latter generates excited formaldehyde. Both species emit radiation when returning to ground state (*Clough and Thrush, 1967; Warren and Babcock, 1970*). The emitted light - in the near IR with $\lambda_{\text{max}} = 1200$ nm for NO₂, in the visible with $\lambda_{\text{max}} = 435$ nm for formaldehyde - is detected by a photomultiplier. At constant reagent gas flow and constant pressure in the measurement cell the light signal is proportional to the ozone concentration in the air sample. Since these systems are very sensitive to reagent and sample flow, these flows have to be both optimised to achieve the peak signal to noise ratio of the detector and, for stability, maintained at constant flow rates. Additionally the sensitivity of the chemiluminescence technique depends on the quality of reagent used. The use of NO instead of ethylene results in enhanced sensitivity and a shorter response time. The instrument exhaust gases must be treated to remove relatively high levels of nitrogen oxides or ethylene, especially if nitrogen oxides or unsaturated hydrocarbons are being measured simultaneously.

The advantages of the chemiluminescence methods for ozone are their fast response times and high sensitivity relative to the UV method. This makes the chemiluminescence suitable for ambient air measurements which require high time resolution (e.g. airborne measurements). However, they are not an absolute method and calibrations are necessary. Due to its relatively complexity, chemiluminescence is not recommended for routine surface ozone measurements at GAW stations. However the chemiluminescence method is a method appropriate for experimental studies of ozone at GAW stations with extended programmes.

C.4 Electrochemical technique used in ozonesondes

The electrochemical techniques used in ozonesondes (*Brewer and Milford, 1960; Kobayashi and Toyama, 1966; Komhyr, 1969*) can also be adopted for ground-based measurements of ozone. The early records from a number of stations in the GAW Global network were made with electrochemical instruments.

The ozone sensor is based on the iodine/iodide redox reaction by ozone, which is performed in an electrochemical cell. As ozone-containing air passes through a buffered KI solution in the cathode half cell, ozone quantitatively oxidises iodide (I⁻) to iodine (I₂). An electrochemical potential is formed across an external circuit by the presence of the I₂, and in order to regain equilibrium, two electrons flow in the external circuit and the I₂ is reduced back to iodide at the platinum cathode. At the same time a suitable anode reaction occurs which can involve iodide, silver or mercury.



The current flow in the external circuit can be, via Faraday's laws of electrolysis, translated into a flow of ozone into the solution and, from the volumetric gas flow rate and its temperature and pressure, the measured electrical current can be converted to an ozone mole fraction. In principle this method is an absolute one, however, impurities in solutions cause a zero current which has to be determined separately.

Intercomparison studies (*Smit et al., 2007*) have shown that in the troposphere ECC-sondes, which are utilizing this measurement technique, can achieve a precision of about 5% with an accuracy better than 10%. For non-ECC sondes the precision and accuracy in the troposphere is less.

The advantage of electrochemical method is the low price, small dimensions and light weight. Disadvantages are intensive maintenance compared to the UV-method, interference by SO₂, H₂O₂, NO₂ and other oxidising or reducing trace gases and much greater measurement uncertainty compared to the ultraviolet method. These techniques are not recommended for routine surface ozone measurements at GAW stations.

C.5 Cavity ring-down spectroscopy with NO titration

Cavity ring-down spectroscopy (CRDS) has been successfully used for measurements of many atmospheric species. However, this technique is not optimal for measuring ozone because its strongest absorption bands occur in the ultraviolet spectral region, where Rayleigh and Mie scattering cause significant cavity losses and dielectric mirror reflectivities are limited (*Washenfelder et al., 2011*). CRDS analysers can be used for measuring ozone indirectly via the complete titration of the ozone with added nitric oxide (NO). The ambient air contains O_{3a}, NO_{2a} and NO_a, where the subscript “a” indicates ambient concentrations. An excess of NO, compared with that just required to titrate all the O₃, is added to the ambient air and new concentrations O_{3t}, NO_{2t} and NO_t, represented by the subscript “t” are rapidly reached. By definition, due to the titration, O_{3t} = 0 and NO_{2t} - NO_{2a} = O_{3a}. Thus by measuring NO₂ before and after the titration and taking the difference, with the measurement either simultaneously in two channels or consecutively in one channel, the ozone mole fraction may be determined. The limit of detection for O₃ is 26 ppt (2 sigma precision) at 1 s time resolution (*Washenfelder et al., 2011*). Current commercially available CRDS instruments for NO₂ show a detection limit of about 50 ppt for NO₂ and do not include the option for ozone measurement. There is a special consideration in calibration of this type of instrument (NO titration). Systems which rely on titration with NO are generally calibrated with gas standards in cylinders, the value of which was assigned gravimetrically. Comparisons between UV photometry and titration with NO have shown that a 2% to 3% bias exists between the techniques (*Tanimoto et al., 2006; Viallon et al., 2006b*). This discrepancy is still unresolved and the CRDS with NO titration method should be calibrated with traceability to primary standard/instrument for measurements within the GAW Programme.

The CRDS with NO titration is an experimental method with promise for future observations and should be incorporated into experimental studies of ozone measurements at selected GAW stations where appropriate.

C.6 Differential optical absorption spectroscopy

Differential Optical Absorption Spectroscopy (DOAS) is a ground-based remote sensing method suitable for observations of several trace substances. The instrument consists of a light source, a long ambient air open optical path generally between 100 m and several km, a retro-reflector and a spectrometer with a telescope, housed with the light source. The spectrometer observes the light source via the retro-reflector. The DOAS system uses Beer’s law, as described in Sections 5, 6 and 7 to determine the ozone concentration (averaged over the light path). In principle DOAS should be a sensitive technique, but this is confounded by the inability of the system to regularly measure a definitive zero and determine the contribution of other UV absorbing gases and aerosol to the observed signal. The DOAS may be used as an experimental technique. DOAS is not recommended for routine surface ozone measurements at GAW stations.

C.7 Multi-axis differential optical absorption spectroscopy

Multi-Axis Differential Optical Absorption Spectroscopy (MAXDOAS) is a ground-based remote sensing method for observations of several trace substances. While this method is suitable for stratospheric monitoring, it is also possible to apply it for trace gas profiles measurements in the upper and lower troposphere. However, since the retrieval procedures as well as possible tropospheric interferences are more complicated in the lower troposphere, it needs highly

experienced personnel for extracting and calculating the mole fractions for the respective trace gases out of the various spectra.

MAXDOAS measurements of ozone, nitrogen dioxide, formaldehyde, bromine monoxide and other species are recommended especially for providing a link between ground-based and satellite measurements at selected GAW stations with extended research programmes. MAXDOAS is not recommended for routine surface ozone measurements at GAW stations.

C.8 Tropospheric ozone lidar

LIDAR (Light Detection and Ranging) is a ground-based remote sensing method for observations of several trace substances. For tropospheric ozone measurements, a LIDAR typically uses two or more wavelengths between 266 nm and 295 nm (*Pelon and Megie, 1982; Browell et al., 1998*). The chosen wavelengths are shorter than the ones used for stratospheric ozone detection (typically between 308 and 353 nm). Compared to the stratosphere, higher ozone absorption efficiency is necessary in the troposphere in order to get enough sensitivity because of the lower ozone mixing ratios in the troposphere compared to the stratosphere. Too much absorption means that most light is extinguished at lower elevations, making it difficult to collect measurement signals from higher elevations. The extreme dynamic range of the back-scattering signal over the troposphere (some decades over a few kilometres of height) is a major technical problem. Facing that, tropospheric ozone LIDAR instruments are more complicated than stratospheric ozone LIDARs and there are fewer systems doing routine observations (*Baray et al., 1999; Papayannis et al., 1999; McDermid et al., 2002*). Typically a tropospheric ozone LIDAR has an accuracy of 2 to 10%, a height resolution in the range of 10 to 100 meters, and a time resolution ranging from a few minutes to 30 minutes for most of the troposphere. In the tropopause region accuracy drops off to 10 to 100%, height resolution degrades to 100 to 1000 m, time resolution gets to hours. Significant interference occurs at pronounced aerosol layers. There, it is difficult to distinguish between aerosol scattering effects and ozone absorption (*Steinbrecht and Carswell, 1995; Browell et al., 1998*). Clouds also pose a substantial problem, because measurements above a thick cloud layer are impossible. A substantial advantage of the LIDAR method (as with stratospheric LIDAR instruments) is due to the double differential measurement principle (wavelength and height): 1) The wavelengths are very well defined by the lasers used. 2) Measured light is compared between two different heights, but has passed through the same equipment. In principle, this eliminates all instrumental constants and makes the LIDAR measurement almost self-calibrating (*Pelon and Megie, 1982; Browell et al., 1998*).

LIDAR tropospheric ozone measurements are recommended especially for providing a link between ground-based and satellite measurements at selected GAW stations with extended research programmes. LIDAR is not recommended for routine surface ozone measurements at GAW stations.

C.9 Other techniques

In recent years, low-cost and small ozone analysers equipped with electrochemical and semiconductor sensors became commercially available. First systematic tests have shown that it is difficult to meet GAW DQOs with the current instrumentation and have also revealed significant interferences mainly due to atmospheric water vapour. Further comprehensive tests are also required to assess the long-term stability of these types of sensors.

D. OTHER PLATFORMS FOR TROPOSPHERIC OZONE MEASUREMENTS

D.1 Ozonesondes

Ozonesondes, which were initially developed to study stratospheric ozone, provide some of the longest data records of tropospheric ozone (Logan, 1999). An ozonesonde consists of a potassium iodide-based ozone sensing device, which is flown on a meteorological balloon and is interfaced to a standard meteorological radiosonde for data transmission. Normally data are taken during a 5 m s^{-1} ascent to a balloon burst altitude of 30-35 km. Flights from a site are typically once per week. Three major types of ozonesondes are presently in use, i.e. electrochemical concentration cell (ECC) after Komhyr (1969), Brewer-Mast (BM) (Brewer and Milford, 1960), and the carbon iodine cell (KC96) (Kobayashi and Toyama, 1966). Nowadays more than 80% of the GAW ozone sounding network uses ECC-type ozonesondes.

Measurement guidelines for ozonesondes are determined by the GAW SAG on Ozone. The techniques and procedures used, and other related information are provided in GAW Report No. 201: Quality Assurance and Quality Control for Ozonesonde Measurements in GAW (in press). In the troposphere ECC-sondes can achieve a precision of about 5% with accuracy better than 10% (Smit *et al.*, 2007). However, even small instrumental differences or the change of chemical composition of the sensing solutions can introduce artifacts in the measured ozone data.

There have been many studies comparing tropospheric ozone measurements from surface stations and ozonesondes (Chevalier *et al.*, 2007; Brodin *et al.*, 2011; Logan *et al.*, 2012).

D.2 Aircraft observations

There have been a number of aircraft-based programmes that measure ozone in the troposphere. Aircraft are fitted with automatic instruments to measure ozone vertical profiles during ascent and descent as well as “flight level” data in the upper troposphere and lower stratosphere. Examples of the programmes are: GASP that operated in the 1970’s (Schnadt-Poberaj *et al.*, 2009); MOZAIC (<http://mozaic.aero.obs-mip.fr/web/>; Marengo *et al.*, 1998; Thouret *et al.*, 1998) that has operated since the early 1990s; and CARABIC (<http://www.caribic-atmospheric.com/>) that has operated since the early 1990s (Brenninkmeijer *et al.*, 1999; Zahn *et al.*, 2002). Since 2011, MOZAIC and CARABIC are being replaced by the IAGOS initiative (<http://www.iagos.org/>), which aims at establishing a fully operational infrastructure for routine measurements from up to 20 passenger aircraft operating from several countries worldwide.

The MOZAIC ozone analysers are similar to the ground-based instruments used in the GAW network. QA/QC procedures in MOZAIC include in-flight performance checks with a built-in ozone source, regular calibration of the ozone analysers during maintenance, typically every 12 months, against a reference instrument traceable to a standard held by the Laboratoire national de métrologie et d’essais, France. The MOZAIC database in Toulouse stores data from more than 30,000 long-distance flights.

Aircraft observations of tropospheric ozone have been integrated with GAW surface observations in a number of studies (Chevalier *et al.*, 2007; Logan *et al.*, 2012).

D.3 Satellite retrievals

Satellite measurements have the distinct advantage that they provide coverage up to global scale. The particular challenge for satellite measurements is that tropospheric ozone makes up only 10% of the total atmospheric ozone and is beneath the stratospheric ozone layer and is thus challenging to be measured from space. In most cases satellite tropospheric ozone is a secondary data product derived from a combination of total column ozone measurements and a measurement that can be used to determine stratospheric ozone (Fishman *et al.*, 1990; Ziemke *et al.*, 1998; Sierk *et al.*, 2006). Another variant is to determine tropospheric ozone from nadir profile retrievals directly

(Liu *et al.*, 2005; Worden *et al.*, 2007; Keim *et al.*, 2009). The vertical resolution is on the order of 10 km in the UV retrieval and about 6 km for infrared observations. UV measurements have rather low sensitivity in the planetary boundary layer. Some tropospheric ozone features derived from a combination of the Ozone Monitoring Instrument (OMI) and the Microwave Limb Sounder (MLS) on the NASA EOS- AURA satellite are shown in Figure 12.

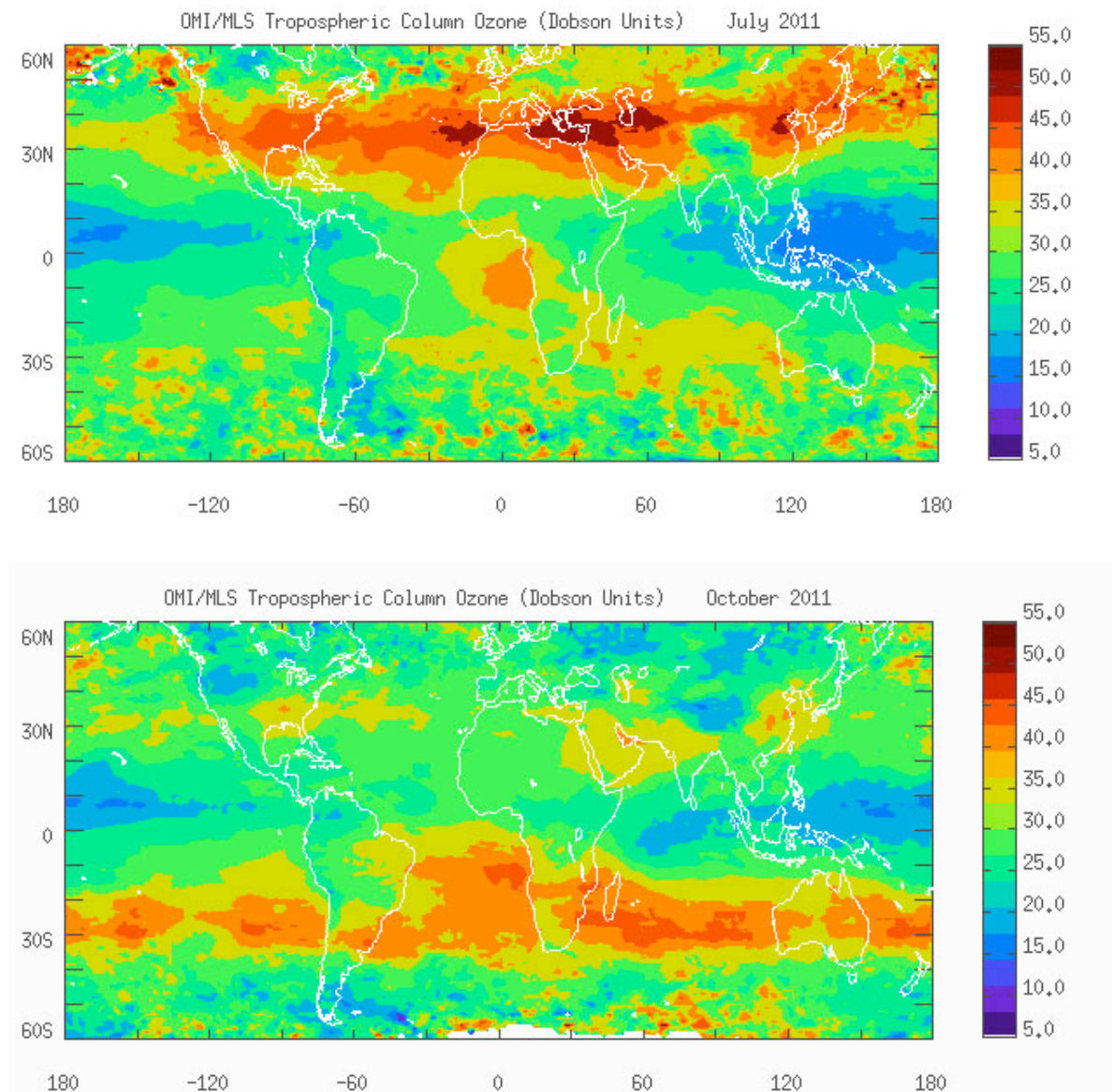


Figure 12 - An example of tropospheric ozone columns determined by residual from OMI observations of total column O_3 and MLS observations of stratospheric O_3 . Values reflect a complex interplay of long-range transport, in-situ chemical production and loss processes, and stratospheric sources (for algorithm please consult Ziemke *et al.*, 2006). Plots are retrieved from http://acd-ext.gsfc.nasa.gov/Data_services/cloud_slice/index.html#nd

Satellite measurements have been very useful in identifying broad-scale features of tropospheric ozone, particularly the extent of continental ozone pollution, the South Atlantic tropospheric ozone maxima off the coast of southern Africa (Fishman *et al.*, 1991) and the oscillation of tropospheric ozone over the Indonesian Archipelago in synchronicity with El Niño (Ziemke *et al.*, 2010).

There has been an absence of comparison of satellite observations of tropospheric ozone with that observed at GAW stations, in part because each system effectively samples different layers of the troposphere.

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Abbreviations and Acronyms

BIPM	International Bureau of Weight and Measures
CCL	Central Calibration Laboratory
CCQM	Consultative Committee for Amount of Substance
CIPM	Comité international des poids et mesures
CMDL	Climate Monitoring and Diagnostics Laboratory, NOAA (now Global Monitoring Division of the Earth System Research Laboratory, NOAA ESRL)
CRDS	Cavity Ring-Down Spectroscopy
CSIRO	Commonwealth Scientific & Industrial Research Organization
DAR	Discovery, Access and Retrieval
DCPC	Data Collection or Production Centre
DQO	Data Quality Objectives
EANet	Acid Deposition Monitoring Network in East Asia
EEA	European Environment Agency
EMEP	European Monitoring and Evaluation Programme
Empa	Swiss Federal Laboratories for Materials Testing and Research
ESRL	Earth System Research Laboratory, NOAA
GAW	Global Atmosphere Watch (WMO Programme)
GAWTEC	GAW Training and Education Centre
GISC	Global Information System Centre
GMD	Global Monitoring Division (as part of NOAA ESRL)
GURME	GAW Urban Research Meteorology and Environment Project
IGACO	Integrated Global Atmospheric Chemistry Observations
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
LS	Laboratory Standard
MACC	Monitoring Atmospheric Composition and Climate Change (EU Project)
MG	Measurement Guidelines
NIST	National Institute of Standards and Technology
NMI	National Metrology Institute, National Measurement Institute
NOAA	National Oceanic and Atmospheric Administration (USA)
NRT	Near-Real-Time
OA	Ozone analyser
PS	Primary Standard
QA	Quality Assurance
QA/SAC	Quality Assurance/Science Activity Centre
QC	Quality Control
RCC	Regional Calibration Centre
RI	Responsible Investigator
SAG	Scientific Advisory Group
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
TS	Transfer Standard
USEPA	United States Environmental Protection Agency
WCC	World Calibration Centre
WDCGG	World Data Center for Greenhouse Gases
WIS	WMO Information System
WMO	World Meteorological Organization

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101. Report of the WMO Workshop on the Measurement of Atmospheric Optical Depth and Turbidity, Silver Spring, USA, 6-10 December 1993, (edited by Bruce Hicks) (WMO TD No. 659).
102. Report of the Workshop on Precipitation Chemistry Laboratory Techniques, Hradec Kralove, Czech Republic, 17-21 October 1994 (WMO TD No. 658).
103. Report of the Meeting of Experts on the WMO World Data Centres, Toronto, Canada, 17 - 18 February 1995, (prepared by Edward Hare) (WMO TD No. 679).
104. Report of the Fourth WMO Meeting of Experts on the Quality Assurance/Science Activity Centres (QA/SACs) of the Global Atmosphere Watch, jointly held with the First Meeting of the Coordinating Committees of IGAC-GLONET and IGAC-ACE, Garmisch-Partenkirchen, Germany, 13 to 17 March 1995 (WMO TD No. 689).
105. Report of the Fourth Session of the EC Panel of Experts/CAS Working Group on Environmental Pollution and Atmospheric Chemistry (Garmisch, Germany, 6-11 March 1995) (WMO TD No. 718).
106. Report of the Global Acid Deposition Assessment (edited by D.M. Whelpdale and M-S. Kaiser) (WMO TD No. 777).
107. Extended Abstracts of Papers Presented at the WMO-IGAC Conference on the Measurement and Assessment of Atmospheric Composition Change (Beijing, China, 9-14 October 1995) (WMO TD No. 710).
108. Report of the Tenth WMO International Comparison of Dobson Spectrophotometers (Arosa, Switzerland, 24 July - 4 August 1995).
109. Report of an Expert Consultation on 85Kr and 222Rn: Measurements, Effects and Applications (Freiburg, Germany, 28-31 March 1995) (WMO TD No. 733).
110. Report of the WMO-NOAA Expert Meeting on GAW Data Acquisition and Archiving (Asheville, NC, USA, 4-8 November 1995) (WMO TD No. 755).
111. Report of the WMO-BMBF Workshop on VOC Establishment of a "World Calibration/Instrument Intercomparison Facility for VOC" to Serve the WMO Global Atmosphere Watch (GAW) Programme (Garmisch-Partenkirchen, Germany, 17-21 December 1995) (WMO TD No. 756).
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