Ambient Air Monitoring Protocol
For PM$_{2.5}$ and Ozone
Canada-wide Standards
for Particulate Matter and Ozone

PN 1456

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The Canadian Council of Ministers of the Environment (CCME) is the major intergovernmental forum in Canada for discussion and joint action on environmental issues of national, international and global concern. The 14 member governments work as partners in developing nationally consistent environmental standards, practices and legislation.
This Monitoring Protocol responds to the commitment by the Canadian Council of Ministers of the Environment (CCME) in the Canada-wide Standards (CWS) for Particulate Matter (PM) and Ozone to establish and maintain a monitoring protocol to ensure the comparability of monitoring data.

This Monitoring Protocol is intended as a reference tool for jurisdictions and the public on the operation and coordination of ambient monitoring programs in support of the CWS for PM and Ozone. Such coordination allows for the analysis of ambient air quality trends, the assessment of regional source-receptor relationships, the analysis of transboundary air quality and the design of implementation plans.

This document was prepared through an open and transparent process by the Working Group on Monitoring and Reporting. The Working Group included representatives from federal, provincial and regional governments as well as participants from health and environmental groups and industry. Following the completion of Joint Actions Implementation and Coordination Committee’s (JAICC) mandate in 2005, the responsibility for completion of the Monitoring Protocol was assigned to the National Air Pollutant Surveillance (NAPS) program. Assistance in document preparation was also provided under contract by ORTECH Environmental.
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EXECUTIVE SUMMARY

The Ambient Air Monitoring Protocol for the Canada-wide Standards (CWS) for PM$_{2.5}$ and Ozone (Monitoring Protocol) should be read in the context of at least two other documents: the Guidance Document on Achievement Determination (GDAD), and the Guidance Document on Keeping Clean Areas Clean and Continuous Improvement (CCME 2007a and b).

The primary purpose of the Monitoring Protocol is to ensure comparability of data across the various ambient monitoring networks in Canada (refer to Section 3) that will be used to achieve the following objectives for the CWS:

- measure representative PM and ozone concentrations in populated areas across the country;
- measure the highest representative ozone concentrations in metropolitan areas;
- measure background concentrations and transport of PM and ozone into areas impacted by transboundary levels;
- support the development of appropriate management strategies on a regional basis;
- track and report attainment progress;
- ensure measurements are reliable and inter-comparative across all regions.

The Monitoring Protocol presents guidelines that will serve as a minimum requirement for networks collecting ambient data in support of the CWS. Adoption of common standards across the country ensures that data collected by networks in different jurisdictions can be analyzed as a consistent dataset, thus increasing the power of statistical methods and gaining maximum scientific return from resources invested. The adoption of national data quality objectives (DQOs) also allows individual networks to exceed those standards where technology and resources permit.

In this document, DQOs are defined as “measurable attributes of the monitoring data that will allow program objectives and measurement objectives to be met.” These performance-based objectives have been defined to allow new and emerging technologies to be incorporated into monitoring activities as they are shown to meet network DQOs.

This Monitoring Protocol identifies four types of monitoring stations:
Table 1: Monitoring strategy for the CWS for PM and ozone

<table>
<thead>
<tr>
<th>Monitoring Station Type</th>
<th>Main Purpose of Monitoring Station</th>
</tr>
</thead>
<tbody>
<tr>
<td>CWS achievement reporting</td>
<td>Tracking and reporting of progress toward meeting the CWS for PM and Ozone.</td>
</tr>
<tr>
<td>Regional transport/background</td>
<td>Demonstrating transboundary influence and influence from background levels and natural events for achievement determination.</td>
</tr>
<tr>
<td>Chemical speciation/precursor</td>
<td>Characterizing air quality and trends, developing and evaluating emission control strategies, estimating health related exposure risks, evaluating source-receptor relationships, providing data for input to run and evaluate models and measuring overall progress of air pollution control programs.</td>
</tr>
<tr>
<td>Special studies</td>
<td>To gain a better understanding of the causes of high PM$_{2.5}$ and ozone concentrations in the ambient air for the development of abatement strategies and conduct health studies, but short term, and may be mobile.</td>
</tr>
</tbody>
</table>

Additional information on the selection of CWS Reporting sites and procedures for determining achievement of CWS target levels is contained in the GDAD.

Quality Assurance/Quality Control (QA/QC) and data management standards are important elements of any monitoring program. The Monitoring Protocol identifies National Air Pollution Surveillance (NAPS) procedures as the standards to be applied to ambient monitoring of PM$_{2.5}$ and ozone. As a minimum, participating networks should meet NAPS Quality Assurance and Quality Control Guidelines (EC, 2004). Jurisdictions are free to exceed national standards where technology and resources permit.

The field of ambient air monitoring is complex, and technology is evolving rapidly. The Monitoring Protocol identifies national standards. The guidelines associated with these standards may need to be revised or supplemented from time to time. The National Air Pollution Surveillance (NAPS) Managers group is recognized as the appropriate body to revise ambient air monitoring protocols for CWS.
# ACRONYMS AND ABBREVIATIONS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAQS</td>
<td>Analysis and Air Quality Section (Environment Canada)</td>
</tr>
<tr>
<td>ARM</td>
<td>approved regional methods (U.S.)</td>
</tr>
<tr>
<td>BAM</td>
<td>beta attenuation mass</td>
</tr>
<tr>
<td>CAPMoN</td>
<td>Canadian Air and Precipitation Monitoring Network</td>
</tr>
<tr>
<td>CCME</td>
<td>Canadian Council of Ministers of the Environment</td>
</tr>
<tr>
<td>CFR</td>
<td>code of federal regulations (U.S.)</td>
</tr>
<tr>
<td>CO</td>
<td>carbon monoxide</td>
</tr>
<tr>
<td>CWS</td>
<td>Canada-wide Standards</td>
</tr>
<tr>
<td>$^{14}$C</td>
<td>carbon-14 or radiocarbon (radioactive isotope)</td>
</tr>
<tr>
<td>DQOs</td>
<td>data quality objectives</td>
</tr>
<tr>
<td>EDXRF</td>
<td>energy dispersive X-ray fluorescence</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency (U.S.)</td>
</tr>
<tr>
<td>ETSC</td>
<td>Environmental Science and Technology Centre (Environment Canada)</td>
</tr>
<tr>
<td>FDMS®</td>
<td>filter dynamic measurement system</td>
</tr>
<tr>
<td>FEM</td>
<td>federal equivalent method (U.S.)</td>
</tr>
<tr>
<td>FR</td>
<td>federal registrar (U.S.)</td>
</tr>
<tr>
<td>FRM</td>
<td>federal reference method (U.S.)</td>
</tr>
<tr>
<td>GDAD</td>
<td>Guidance Document on Achievement Determination (CWS)</td>
</tr>
<tr>
<td>HAMN</td>
<td>Hamilton Air Monitoring Network</td>
</tr>
<tr>
<td>HNO₃</td>
<td>nitric acid</td>
</tr>
<tr>
<td>IMPROVE</td>
<td>Interagency Monitoring of Protected Visual Environments (U.S.)</td>
</tr>
<tr>
<td>KCAC/CI</td>
<td>Keeping Clean Areas Clean – Continuous Improvement (CWS)</td>
</tr>
<tr>
<td>Kpa</td>
<td>kilopascal</td>
</tr>
<tr>
<td>MARS</td>
<td>Measurement and Analysis Research Section (Environment Canada)</td>
</tr>
<tr>
<td>MeV</td>
<td>mega electron-volt</td>
</tr>
<tr>
<td>MSC</td>
<td>Meteorological Service of Canada</td>
</tr>
<tr>
<td>MnO₂</td>
<td>manganese dioxide</td>
</tr>
<tr>
<td>MOE</td>
<td>Ministry of the Environment (Ontario)</td>
</tr>
<tr>
<td>MRWG</td>
<td>Monitoring and Reporting Working Group (CCME)</td>
</tr>
<tr>
<td>NAAQO</td>
<td>National Ambient Air Quality Objectives (Canada)</td>
</tr>
<tr>
<td>NAAQS</td>
<td>National Ambient Air Quality Standards (U.S.)</td>
</tr>
<tr>
<td>NAPS</td>
<td>National Air Pollution Surveillance</td>
</tr>
<tr>
<td>NARSTO</td>
<td>formally North American Research Strategy for Tropospheric Ozone</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>ammonium nitrate</td>
</tr>
<tr>
<td>NH₃</td>
<td>ammonia</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology (U.S.)</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>nitrate</td>
</tr>
<tr>
<td>NAPS RM</td>
<td>NAPS reference method</td>
</tr>
<tr>
<td>nm</td>
<td>nanometre</td>
</tr>
<tr>
<td>NO</td>
<td>nitric oxide</td>
</tr>
<tr>
<td>NO₂</td>
<td>nitrogen dioxide</td>
</tr>
<tr>
<td>NOy</td>
<td>total reactive oxidized nitrogen species</td>
</tr>
<tr>
<td>PAMS</td>
<td>photochemical assessment monitoring stations (U.S.)</td>
</tr>
<tr>
<td>PAN</td>
<td>peroxyacetyl nitrate</td>
</tr>
<tr>
<td>PBMS</td>
<td>performance-based measurement system</td>
</tr>
<tr>
<td>PM</td>
<td>particulate matter</td>
</tr>
<tr>
<td>PM₂.₅</td>
<td>particulate matter less than or equal to 2.5 microns in diameter (aka PM fine fraction)</td>
</tr>
<tr>
<td>Term</td>
<td>Description</td>
</tr>
<tr>
<td>------------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>PM&lt;sub&gt;10&lt;/sub&gt;</td>
<td>particulate matter less than or equal to 10 microns in diameter</td>
</tr>
<tr>
<td>PM&lt;sub&gt;10-2.5&lt;/sub&gt;</td>
<td>particulate matter in the size range 2.5 to 10 microns in diameter (aka PM coarse fraction)</td>
</tr>
<tr>
<td>ppb</td>
<td>parts per billion</td>
</tr>
<tr>
<td>QA/QC</td>
<td>quality assurance/quality control</td>
</tr>
<tr>
<td>RH</td>
<td>relative humidity</td>
</tr>
<tr>
<td>SCC</td>
<td>sharp cut cyclone</td>
</tr>
<tr>
<td>SHARP</td>
<td>synchronized hybrid ambient real-time particulate</td>
</tr>
<tr>
<td>SLEA</td>
<td>Sarnia Lambton Environmental Association</td>
</tr>
<tr>
<td>SOP</td>
<td>standard operating procedure</td>
</tr>
<tr>
<td>SO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>sulphur dioxide</td>
</tr>
<tr>
<td>SSI</td>
<td>size selective inlet</td>
</tr>
<tr>
<td>STP</td>
<td>standard temperature and pressure</td>
</tr>
<tr>
<td>SVOC</td>
<td>semi-volatile organic compounds</td>
</tr>
<tr>
<td>SVPM</td>
<td>semi-volatile particulate matter</td>
</tr>
<tr>
<td>TEOM&lt;sup&gt;TM&lt;/sup&gt;</td>
<td>tapered element oscillating microbalance&lt;sup&gt;TM&lt;/sup&gt;</td>
</tr>
<tr>
<td>TSP</td>
<td>total suspended particulate</td>
</tr>
<tr>
<td>VSCC&lt;sup&gt;TM&lt;/sup&gt;</td>
<td>very sharp cut cyclone</td>
</tr>
<tr>
<td>VOC</td>
<td>volatile organic compounds</td>
</tr>
<tr>
<td>WINS</td>
<td>well impaction ninety-six</td>
</tr>
<tr>
<td>μg/m&lt;sup&gt;3&lt;/sup&gt;</td>
<td>microgram per cubic metre</td>
</tr>
</tbody>
</table>
INTRODUCTION

1.1 Purpose and Application

This document provides guidance for the federal, provincial and territorial governments to ensure the coordination of monitoring data. The Ambient Air Monitoring Protocol for PM$_{2.5}$ and Ozone allows for better coordination of the design and operation of monitoring programs, analyses of ambient air quality trends, assessments of regional source-receptor relationships, analyses of transboundary air quality impacts, and design of implementation plans. For brevity, this document is hereafter referred to as the Monitoring Protocol.

Other ambient air monitoring-related documents specifically prepared for the Canadian Council of Ministers of the Environment (CCME) to support the management of the Canada-wide Standards for PM and Ozone (CWS) include:

- Guidance Document on Achievement Determination (GDAD); and
- Guidance Document on Keeping Clean Areas Clean and Continuous Improvement.

The primary purpose of the Monitoring Protocol is to ensure comparability of data across the various ambient monitoring networks in Canada (refer to Section 3) that will be used to achieve the following objectives of the CWS for PM and Ozone:

- measure representative PM and ozone concentrations in populated areas across the country;
- measure the highest representative ozone concentrations in metropolitan areas;
- measure background concentrations and transport of PM and ozone into areas impacted by transboundary levels;
- support the development of appropriate management strategies on a regional basis;
- track and report progress on achievement of the numerical targets;
- ensure measurements are reliable and inter-comparative across all regions.

Quality Assurance/Quality Control (QA/QC) and data management standards are important elements of any monitoring program. The Monitoring Protocol identifies National Air Pollution Surveillance (NAPS) procedures as the standards to be applied to ambient monitoring of PM$_{2.5}$ and ozone. As a minimum, participating networks should meet NAPS Quality Assurance and Quality Control
Guidelines (EC, 2004). Jurisdictions are free to exceed national standards where technology and resources permit.

Participating ambient air monitoring networks should operate in a manner consistent with the methods and practices described in this Monitoring Protocol at all sites from which data will be used to address the CWS objectives described above. Data comparability is essential for analyzing ambient air quality trends, assessing regional source-receptors and analyzing transboundary air quality. Adherence to Monitoring Protocol specifications is particularly important at sites specifically designated for tracking and reporting, as described in Section 4. The Monitoring Protocol follows, and supersedes, Appendix B of the Ambient Air Monitoring Working Group’s *Ground-Level Ozone and Precursor Monitoring Guidelines and Implementation Report*. (Canadian – Monitoring, 1997).

### 1.2 Background to Canada-wide Standards for PM and Ozone

On June 5, 2000, the CCME, except Quebec, endorsed the CWS for PM and Ozone. The CWS Agreement recognizes that PM and ozone negatively affect human health and the environment in a significant way, and it establishes the need for a nationally coordinated, long-term management toward minimizing risks from these pollutants.

In agreeing to the CWS, federal, provincial and territorial jurisdictions across Canada have made strong commitments to implement the CWS, to share information respecting implementation, and to be accountable to their respective publics.

The CWS Agreement consists of several parts:

- Part 1 establishes numerical targets and timeframes for achieving the goals within each jurisdiction.
- Part 2 establishes the steps each jurisdiction will take toward implementation of plans, programs and actions to meet the standards within agreed-to timeframes, sets out provisions for subsequent reviews of the standards, and prescribes substance and timing for jurisdictions to report on their progress in meeting the standards.
- Annex A acknowledges the need to take preventative action in many areas of the country, with provisions for developing strategies such as Continuous Improvement and Keeping Clean Areas Clean.
- Annex B provides direction for jurisdictional reporting on all aspects of the CWS, from management plans and actions to achievement of the numerical targets.

#### Standards to be Achieved by 2010

Under the CWS, jurisdictions defined ambient Standards for fine particulate matter (PM$_{2.5}$) and ozone to be achieved by 2010. The Standards are recognized as an important first step toward the long-term goal of minimizing the risks that PM and ozone pose to human health and the environment. The Standards and their statistical forms are as follows:

- **PM$_{2.5}$ CWS** – 30 μg/m$^3$ as a 24-hour average
  
  The *form of the Standard* is the 3-year average of the annual 98th percentile 24-hour average PM$_{2.5}$ levels.

- **Ozone CWS** – 65 ppb as an 8-hour average
  
  The *form of the Standard* is the 3-year average of the annual 4th highest of the daily maximum 8-hour average ozone levels.
At the time the CWS were endorsed, these Standards represented a balance between a desire to achieve the best health and environmental protection possible in the near term, and the feasibility and costs of reducing the smog-producing emissions.

The PM$_{2.5}$ and ozone Standards can be viewed as consisting of two parts. The first part expresses the numerical values themselves, that is 30 µg/m$^3$ for PM$_{2.5}$ and 65 ppb for ozone, and the second part is the *form* of the Standards. The form of the Standards states how the measured PM$_{2.5}$ and ozone levels are to be expressed for evaluating whether the Standards are being achieved or not. These forms are the specified 3-year averages.

The reporting provisions in Part 2 of the CWS Agreement commit jurisdictions to report as follows on progress towards meeting the numerical targets and timeframes, implementation of emission reduction plans and programs, and review of the standards:

(a) to the respective publics of each jurisdiction on a regular basis, the timing and scope of reporting to be determined by each jurisdiction;

(b) to Ministers and the public, with comprehensive reports at 5-year intervals beginning in 2006, and reports on achievement and maintenance of the CWS annually, beginning in 2011, in accordance with guidance provided in Annex B.

Annex A applies to those parts of Canada that do not exceed the CWS targets. The annex describes the goals of Continuous Improvement and Keeping Clean Areas Clean and encourages jurisdictions to apply pollution prevention and best management practices to achieve these goals.

Annex B, the Reporting Protocol, contains provisions designed to help jurisdictions ensure consistency and comparability in their reporting, and to help the public better understand how jurisdictions plan to track and report on progress. To help meet these objectives, the CCME committed to the preparation and update, as required, of a *Guidance Document on Achievement Determination* (GDAD) for the PM and Ozone CWS.

The Reporting Protocol also commits jurisdictions to maintain their own data on ambient measurements of PM$_{2.5}$, PM$_{10}$ and ozone and to make the data accessible to the public. Ambient air monitoring experts in Canada are to establish and maintain a Monitoring Protocol (this document) to ensure the national comparability of such monitoring data. This allows for better coordination of monitoring program design and operation, ambient air quality trends analyses, regional source-receptor assessments, transboundary air quality analyses and implementation plan design.

For further reference, the CWS Agreement is available online at www.ccme.ca.
2. POLLUTANTS OF INTEREST

The Canada-wide Standards for PM and Ozone focus specifically on the measurement of ambient concentrations of PM$_{2.5}$ and ground-level ozone in air, primarily for the purpose of determining achievement of the CWS numerical targets. Another important objective for monitoring is to develop improved source-receptor relationships and a better understanding of the causes of high ambient concentrations of PM$_{2.5}$ and ozone for abatement strategy development. This not only requires monitoring of PM$_{2.5}$ and ozone, but must also include their precursors and the chemical composition of PM$_{2.5}$.

Ozone is formed as a secondary pollutant in the atmosphere whereby concentrations are highly dependent on solar radiation and ambient concentrations of nitrogen oxides (NO$_X$), volatile organic compounds (VOC), and carbon monoxide (CO). In rural areas, NO$_X$ generally makes up only a small fraction of total reactive oxidized nitrogen species (generally referred to as NO$_Y$ and including peroxyacetyl nitrate (PAN), HNO$_3$ and NO$_3^-$ aerosol along with NO and NO$_2$). Speciated VOC measurements provide information on the contribution of the principal VOC emissions sources to ambient concentrations which may in turn be used to verify emissions inventories and photochemical modelling results. Carbon monoxide is an important component in oxidant photochemistry and ground-level ozone formation. In urban areas, CO measurements provide an index of anthropogenic emissions and, when linked with NO$_X$ and VOC measurements, can provide important information related to emissions verification and the efficiency of emissions controls, especially as they relate to the transportation sector. In rural settings, CO provides an index of the level of anthropogenic influence on air mass chemistry and, to some degree, the age of the air mass.

PM$_{2.5}$ is composed of a mixture of primary and secondary particles, which have long lifetimes in the atmosphere (days to weeks) and can travel long distances (hundreds to thousands of kilometers). Sulphate, nitrate, organic and elemental carbon, trace elements, ammonium and water are often the major constituents of PM$_{2.5}$. Primary particles are emitted directly into the atmosphere and include soil-related particles and carbon particles from fossil fuel combustion and biomass burning. Combustion processes also emit primary particles consisting of mixtures of many trace metal compounds. The principal types of secondary aerosols are ammonium sulphate and nitrate, formed from gaseous emissions of SO$_2$ and NO$_X$ that react with ammonia (NH$_3$), as well as organics formed from volatile and semi-volatile organic compounds. While the inorganic precursor gas relationships are more predictable, the extent to which VOCs contribute to PM$_{2.5}$ formation is not well understood and additional measurement data are needed to quantitatively link specific source types to ambient PM$_{2.5}$ concentrations.

The coarse inhalable particle size fraction, PM$_{10-2.5}$, consists of more localized fugitive dust which usually travels lesser distances than finer particle sizes and represents an important urban air quality parameter. Periodic natural events (e.g., dust storms, forest fires) can also contribute to elevated background levels.
This parameter differs in origin, composition and atmospheric behaviour with respect to the other more diffusive precursor constituents, but has linkages since potential carbonaceous constituents and light scattering properties of coarse particles can be relevant to changes in solar radiation.

Figure 1, taken from Chapter 6 of *Precursor Contributions to Ambient Fine Particulate Matter in Canada* (EC, 2001), is a simplified schematic of the processes that lead to formation of secondary PM$_{2.5}$. The diagram is helpful in identifying the importance of carrying out complementary and collocated measurements in addition to PM$_{2.5}$ mass concentrations and ozone mixing ratio at a subset of sites.

**Figure 1: Simplified Secondary Particle Formation Processes**

As documented by NARSTO (a public/private partnership dedicated to improving management of air quality in North America) and elsewhere, both climatology and meteorology affect essentially all of the processes related to particulate matter formation, dispersive transport and deposition losses. Accordingly, the understanding of PM$_{2.5}$ and precursor compound relationships requires associated measurements of meteorological parameters: wind speed, wind direction, temperature, relative humidity and solar radiation at pertinent locales. Seasonal concentration differences amongst the various parameters are often evident from monitoring data but not always readily explainable from available emissions data. It is known that large-scale PM$_{2.5}$ episodes are caused mainly by unusual meteorological conditions such as the accumulation of precursor emissions associated with summer high pressure systems characterized by high temperatures, low wind speeds and stable conditions. Stagnating air masses during winter, in conjunction with lower temperatures, also facilitates the formation of secondary inorganic nitrate particle components.

General concentration trends and temporal distributions, for specific parameters in Canada, are noted in Table 2. Temporal patterns may sometimes differ spatially depending on contributions of local and transported pollutants and meteorological variations.
Table 2: General Urban Parameter Trends and Temporal Features

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Annual Mean (or other) Concentration Trend</th>
<th>Trend Period</th>
<th>Seasonal Distribution</th>
<th>Diurnal or Daily Features</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_{2.5}$</td>
<td>minor decrease to no apparent change in some cities</td>
<td>1986-1998</td>
<td>typically higher in summer but not all regions</td>
<td>typically highest on weekday mornings</td>
<td>EC 2001 EC 2005a NARSTO 2003</td>
</tr>
<tr>
<td>PM$_{10.25}$</td>
<td>generally decreasing</td>
<td>1984-2000</td>
<td>higher in summer</td>
<td>highest on weekdays</td>
<td>CCME 2003</td>
</tr>
<tr>
<td>CO</td>
<td>maximum concentrations generally decreasing in Ontario</td>
<td>1990-2003</td>
<td>generally highest in winter</td>
<td>highest in morning and late afternoon at urban sites</td>
<td>MOE 2004 EC 2005b</td>
</tr>
<tr>
<td>VOC</td>
<td>species dependent, some aromatics decreasing, decreasing</td>
<td>1992-1999</td>
<td>aromatic species generally highest in winter but variable in East</td>
<td>highest aromatics in morning and lowest at mid-day for single urban (continuous monitor) site</td>
<td>EC 2001 MOE 2004 SLEA 2006</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>NA</td>
<td>NA</td>
<td>highest in spring, summer and autumn</td>
<td>NA</td>
<td>EC 2001</td>
</tr>
</tbody>
</table>
Ambient air quality monitoring is conducted by both government and industry in Canada. All three levels of government (federal, provincial/territorial, regional/municipal) have monitoring programs established.

At the federal level, Environment Canada is the department responsible for measuring pollution levels in the air. The Department has established several ambient air quality monitoring networks that focus on separate air issues.

The National Air Pollution Surveillance (NAPS) Network is a federal–provincial/territorial/regional government program that manages a national network of air pollution monitoring stations primarily located in Canadian urban centres. The federal government is responsible for coordinating the activities in the network, providing instrumentation, standardizing methods and procedures, ensuring quality assurance, carrying out audits and publishing NAPS data. The provinces and participating regional governments provide on-site operation and maintenance of the stations, quality assurance and quality control, data collection and data validation.

The NAPS network collaborating agencies are the following:
- Newfoundland and Labrador Department of Environment and Conservation
- Prince Edward Island Department of Environment, Energy and Forestry
- Nova Scotia Environment and Labour
- New Brunswick Department of the Environment / Ministère de l'Environnement du Nouveau-Brunswick
- Ministère du Développement durable, de l'Environnement et des Parcs du Québec
- Ville de Montréal
- Ontario Ministry of Environment
- Manitoba Conservation
- Saskatchewan Ministry of Environment
- Alberta Environment
- British Columbia Ministry of the Environment
- Metro Vancouver
- Government of Yukon
- Government of the Northwest Territories
- Government of Nunavut / Gouvernement du Nunavut
- Environment Canada
While NAPS is the most prominent network, Environment Canada has also established or takes part in other networks. The Canadian Air and Precipitation Monitoring Network (CAPMoN) is a non-urban air quality monitoring network with siting criteria designed to ensure that the measurement locations are regionally representative and are not affected by local sources of air pollution. CAPMoN has been in operation for more than 20 years. Its initial focus was on acid rain, but now some sites also measure smog pollutants (NO\textsubscript{X}, PM and ozone). Data from the CAPMoN are used to assess regional background levels and long-range transport of pollutants.

The provinces have legislative authority to control air pollution, and therefore most have established monitoring sites to measure both ambient air quality as well as acid deposition.

Alberta has several airshed associations responsible for monitoring and reporting on air quality within a designated area. Airshed associations are comprised of industry, government and non-government organizations using a consensus model to make decisions.

Some regional/municipal governments have established monitoring networks as well such as: Metro Vancouver (formerly the Greater Vancouver Regional District (GVRD)) in British Columbia and the Ville de Montréal in Quebec who both measure ambient air pollutants.

Industry also conducts ambient air quality monitoring in Canada. These sites are established close to their facilities and are usually required under provincial operating permits. Community monitoring networks, operated by local industry groups, include the Sarnia Lambton Environmental Association (SLEA) network, the Hamilton Air Monitoring Network (HAMN) and the Sudbury monitoring network.
The number and distribution of air quality monitoring stations required in a network depend on the area to be covered, the spatial variability of the pollutants being measured, and the required data usage.

Monitoring networks including NAPS are generally designed to help assess the primary integrated air quality influences pertaining to population exposure and/or ecological effects; these influences include emission source contributions and atmospheric processes. In most instances, a subset of existing NAPS or CAPMoN network sites should be applicable to CWS requirements. For CWS implementation, jurisdictions will review the current monitoring networks to determine and designate the most applicable sites for reporting as well as define any necessary modifications or additional monitors that are needed to meet the monitoring requirements for CWS achievement determination. From an effects perspective, it is relevant to note that network monitoring data trends can be used, with reasonable accuracy, to evaluate associated potential trends in effects, but it is ultimately more difficult to quantify concentration thresholds related to specific effects (Sajani et al 2004).

### 4.1 Monitoring Network Objectives

The most important consideration in designing or implementing any monitoring system is defining its overall objectives. Although similar measurement methods and protocols can be used to collect PM$_{2.5}$ and ozone data from all sites, the location of sites and their proximity to sources, population centres and political boundaries will vary, depending on the proposed use of the data.

The primary purpose of the Monitoring Protocol is to ensure comparability of data across the various ambient monitoring networks in Canada (refer to Section 3) that will be used to achieve the following objectives of the CWS for PM and Ozone:

- measure representative PM and ozone concentrations in populated areas across the country;
- measure the highest representative ozone concentrations in metropolitan areas;
- measure background concentrations and transport of PM, ozone and their precursors into areas impacted by background/transboundary sources;
- support the development of appropriate management strategies on a regional basis;
- track and report on air quality trends and the effectiveness of management strategies;
- ensure measurements are reliable and inter-comparative across all regions.
4.2 Spatial Representativeness

To satisfy different monitoring objectives, stations are sited by both geographical and physical location. Physical location is defined by the concept of spatial scale of representativeness and is described in terms of the physical dimensions of the air parcel nearest to a monitoring station throughout which actual pollutant concentrations are reasonably uniform. The goal in siting stations is to match the spatial scale represented by the sample of monitored air with the spatial scale most appropriate for the monitoring objective of the station.

Six categories of spatial scales of representativeness have been defined for monitoring station siting purposes (U.S. EPA, 1997)

Table 3: Spatial Scales of Representativeness

<table>
<thead>
<tr>
<th>Category of Spatial Scale</th>
<th>Range of Air Volume of Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microscale</td>
<td>Usually several metres to 0.1 km.</td>
</tr>
<tr>
<td>Middle Scale</td>
<td>Typical of areas up to several city blocks ranging in size from about 0.1 to 0.5 kilometres.</td>
</tr>
<tr>
<td>Neighborhood Scale</td>
<td>Usually within some extended area of the city that has relatively uniform land use with dimensions in the 0.5 to 4.0 kilometres range.</td>
</tr>
<tr>
<td>Urban Scale</td>
<td>Entire metropolitan area ranging in size from 4 to 50 kilometres.</td>
</tr>
<tr>
<td>Regional Scale</td>
<td>Usually a rural area of reasonably homogeneous geography and extends from 10s to 1,000s of kilometres.</td>
</tr>
<tr>
<td>Global Scale</td>
<td>Represent concentrations characterizing a nation and the globe as whole.</td>
</tr>
</tbody>
</table>

4.3 Site Classification

To address the broad application of data described in the CWS, the following four types of monitoring stations are identified:

1. CWS achievement reporting
2. Regional transport/background
3. Chemical speciation/precursor
4. Special studies

4.3.1 CWS Achievement Reporting Stations

Population or community-oriented monitoring sites are used to determine the representative area-wide public exposure levels of PM$_{2.5}$ and ozone. These stations measure PM$_{2.5}$ and ozone for comparison with the
CWS and should be located in residential, commercial, industrial or other areas where people spend significant amounts of time. Neighbourhood or urban scale stations are typically appropriate for this objective.

Measurement at neighbourhood or urban spatial scales should be generally appropriate for PM$_{2.5}$ achievement determination purposes when sub-regional conditions for the dimensional area are reasonably homogeneous with respect to PM$_{2.5}$ concentrations, land-use and land-surface characteristics. Although the highest PM$_{2.5}$ concentrations within communities might be expected to occur near major emission sources, the levels measured close to individual sources may not necessarily represent concentrations to which the majority of the community population is exposed. Selection of associated PM$_{2.5}$ monitoring sites requires careful consideration (guidance is provided in subsequent sections of this document) in order to account for both collective community and other source contributions to the measured levels. Properly sited community-oriented measurements should then facilitate the development of control strategies to reduce broader community-wide exposure to PM.

Ozone is formed in the atmosphere by reactions between its precursor substances, VOC and NO$_X$. It is also depleted by reactions with numerous substances including scavenging by NO.

**Spatial and Temporal Variation of Ozone Concentrations**

Given the complexities of ozone distribution in metropolitan areas, there is a need to determine areas of maximum ozone concentrations by conducting an ozone analysis that considers local sources of precursors, ozone sinks, regional concentrations and meteorology, site elevation and topography.

Following below are several factors known to influence large-scale spatial variation of ozone distribution in metropolitan areas; these factors can also help to identify locations where human health and natural resources could be at risk. This information can be used to optimize future monitoring networks.

- Because ozone is a secondary pollutant, maximum ozone concentrations usually occur 3 to 5 hours after maximum precursor emissions and under conditions of light winds, usually downwind of the urban region. Average wind speeds of 5 km/hr would mean the greatest ozone concentrations would typically show up 15 – 25 km downwind to the major sources of ozone precursors.

- Higher ozone concentrations can occur at upwind sites when regional concentrations are greater than urban concentrations, at higher elevation sites, and in areas where topography and synoptic meteorological conditions are conducive to intrusion of stratospheric ozone into the troposphere.

- Lowest ozone concentrations in a metropolitan area typically occur in the urban centre and in locations near ozone precursor sources. Mid-range concentrations typically occur in neighbourhoods and locations surrounding the urban centre.

Community-oriented measurements are best suited to characterize area-wide exposure levels and the associated population health impacts. Control strategies designed to achieve CWS levels should be aimed at the highest ozone concentrations in a metropolitan area. Therefore, stations designed to measure the maximum ozone concentration in metropolitan areas should be located downwind of precursor source locales on days when the ozone CWS is exceeded or days when conditions are expected to be conducive to ozone formation. For some communities maximum ozone levels may be recorded upwind of the urban core due to ozone scavenging. Neighbourhood or urban-scale stations are appropriate for this objective.

It is important to determine the siting requirements to measure the highest representative ozone concentration in metropolitan areas. Although maximum ozone concentrations, due to the urban sources, may occur beyond the urban area, the most relevant CWS monitoring is intended to measure the highest
Ambient Air Monitoring Protocol for PM$_{2.5}$ and Ozone

4.3.2 Regional Transport/Background Stations

There are two significant regional influences that may be taken into account when determining CWS achievement. First, some areas of Canada are highly impacted by transboundary air pollution; second, high background levels of PM and ozone from natural sources and events occur occasionally throughout the year.

Regional transport/background monitoring is used to determine the upwind concentration of PM$_{2.5}$ and ozone for communities that may be significantly influenced by pollution from transboundary source regions or high background levels. Regional scale stations are typically appropriate for this objective. The GDAD provides the following recommendations regarding the siting of regional transport and background monitors for demonstrating transboundary influence and high background levels.

Transboundary Influence

- Jurisdictions should identify one or more monitoring sites upwind of the non-compliant community in question, located between the community and the major source area that may be affecting it.

- In the case of a community adjacent to the Canada – U.S. border or a border with another province/territory, the measurement site may have to be at a near-border location within the community, upwind of the community core. Similarly, for a community on the shores of a border water body, the measurement site should be sited within the community near the shoreline, upwind of the community core.

- Jurisdictions should measure PM$_{2.5}$ (including chemical speciation for major inorganic ions as a minimum), ozone and local winds at this site using standard methods accepted by the National Air Pollution Surveillance (NAPS) Monitoring Network or the Canadian Air and Precipitation Monitoring Network (CAPMoN).

- If it is likely that precursor pollutants are being transported from the upwind jurisdiction and are contributing to PM$_{2.5}$ or ozone levels in the community, then jurisdictions should measure ambient concentrations of NO, all oxidized nitrogen compounds (NO$_Y$), NH$_3$, SO$_2$ and VOC (including speciation).

Influence from Background or Natural Events

- Jurisdictions should identify one or more monitoring sites upwind of the non-compliant community in question and in a location that is not downwind of any major anthropogenic source area.

- Depending on the pollutant in question, jurisdictions should measure PM$_{2.5}$ (including chemical speciation for major inorganic ions as a minimum), ozone and local winds at this site using standard methods accepted by NAPS or CAPMoN.

- Jurisdictions should also measure ambient concentrations of VOC, including isoprene and terpenes. Isoprene is a primary precursor of ozone, and terpenes are important precursors of the organic component of PM$_{2.5}$.
Additional regional or background monitors may also be sited to extend the geographical coverage beyond the areas represented by CWS reporting sites for both the transboundary region between Canada and the United States and for background/trends information.

### 4.3.3 Chemical Speciation/Precursor Stations

The goals of chemical speciation/precursor monitoring are to:

- assess trends in PM mass components and gaseous precursor concentrations;
- identify specific source contributions in airsheds;
- track the effectiveness of control strategies;
- provide input to air quality models and analyses;
- improve PM and ozone sampling and monitoring strategies;
- provide information for health impact studies;
- measure overall progress of air pollution control programs.

Stations will normally be collocated with PM$_{2.5}$ and/or ozone monitors; the scale of representativeness will therefore vary accordingly.

### 4.3.4 Special Studies Stations

In general, Special Studies sites are sites where intensive monitoring is done across a wide range of atmospheric constituents. The goal of such monitoring is to further develop the science and technology underpinning of the CWS. These sites contribute additional information that could strengthen policy development and program management for PM and ozone.

Special Studies sites can encompass a wide variety of measurement programs and might focus on characterizing emission sources and transformation products, validating model outputs, improving or inter-comparing measurement methods, or understanding health and environmental impacts. These sites would likely undertake speciation of PM$_{2.5}$ samples.

Spatial representativeness of Special Studies sites could vary considerably, depending on specific issues being investigated, and sites may not necessarily be community-oriented.

Vehicle traffic emissions, including exhaust components and re-suspended road dust, can represent an important and sometimes predominant local source contributor of CWS-related parameters in large urban areas. This can affect both the magnitude and variability of urban air pollutant levels, particularly near high traffic routes. Associated assessments are likely best accomplished by special studies, whereas long-term CWS siting, which maintains a distance from specific roadways, should strive to account for collective contributions from this and other urban sources.

### 4.4 Site Selection

The selection of sites to meet the network objectives is based on the requirements for distribution, location, separation and spatial scale of representation (refer to Section 4.2).

Site selection criteria can be divided into those relating to urban and rural monitoring networks. Urban monitoring networks include CWS achievement sites as well as speciation/precursor and special studies.
sites. Rural monitoring networks include background and regional transport sites that may also comprise chemical species and gaseous precursors, and special studies sites.

Along with addressing the overall monitoring objectives, the site selection process needs to take the following practical factors into consideration:

- reliable electric power source
- accessibility throughout the year
- security of the site from unauthorized access and vandalism
- specifications for sampling shelter and inlet probe installation
- possible interference from local sources and plume dispersion effects

4.4.1 Urban Networks

Distribution

The CWS achievement determination requires that the reporting areas (RA) be based on the census metropolitan areas (CMA) and census agglomerations (CA). Larger CMAs (populations >500,000) may be further divided into reporting sub-areas (RSA). Guidance for establishing RA and RSA boundaries is detailed in Section 2 of the GDAD. Although some reporting areas may select more than one monitoring station to report average concentrations of particulate matter, most communities may select a single urban station to report maximum ozone concentrations.

Location

For specific monitoring requirements, a site is selected to provide the most representative air quality information to the population of a given RA or RSA. When a small number of monitoring stations are planned for a community or reporting area, subjective methods are often employed such as: the selection of one site each in industrial, commercial and residential neighbourhoods; or the NAPS (EC, 1988) Station Classification and Distribution Criteria (see Table 4 below). The NAPS criteria were used initially to select urban monitoring locations. Many of these locations remain as monitoring sites today. New or additional NAPS sites are now selected on the basis of the NAPS Quality Assurance and Quality Control Guidelines (2004) in consultation with network agencies to produce air quality data representative of the geographic area of interest. For larger networks, a more objective method of design may be required. Munn (1981) defines two basic methods for network design: a statistical method and a modelling method.
### Table 4: NAPS Network Station Classification and Distribution Criteria

<table>
<thead>
<tr>
<th>Distribution</th>
<th>Separation</th>
<th>Location</th>
<th>Spatial Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NAPS Sites</strong></td>
<td>1 per 250,000 people (with exceptions for regional cities and Territories)</td>
<td>1st site</td>
<td>Downtown</td>
</tr>
<tr>
<td>Maximum 6 sites per urban area</td>
<td>2nd site</td>
<td>Residential with worst air quality</td>
<td>Neighbourhood</td>
</tr>
<tr>
<td></td>
<td>3rd site</td>
<td>Residential with poor air quality at a 90° quadrant from the 1st and 2nd sites</td>
<td>Neighbourhood</td>
</tr>
<tr>
<td></td>
<td>4th site</td>
<td>Secondary commercial with heavy traffic</td>
<td>Middle or Neighbourhood</td>
</tr>
<tr>
<td></td>
<td>5th site</td>
<td>Residential in third quadrant</td>
<td>Neighbourhood</td>
</tr>
<tr>
<td></td>
<td>6th site</td>
<td>Residential in fourth quadrant or third commercial</td>
<td>Neighbourhood</td>
</tr>
<tr>
<td><strong>CWS Designated Urban Sites</strong></td>
<td>Minimum 1 per CMA or CA &gt;100,000 and Reporting Sub-Area (RSA)</td>
<td>1st site</td>
<td>Sited to satisfy CWS reporting requirements and objectives</td>
</tr>
<tr>
<td></td>
<td>1 each for P.E.I., Yukon, Nunavat and Northwest Territories where population &lt;100,000</td>
<td>2nd site</td>
<td>Uniform concentration for the RA for PM$_{2.5}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3rd site</td>
<td>Where possible PM$_{2.5}$ and Ozone monitors to be collocated</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4th site</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5th site</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>6th site</td>
<td></td>
</tr>
<tr>
<td><strong>CWS Designated Upwind Rural Sites</strong></td>
<td>1 or more sites per CMA or CA</td>
<td>To assess transboundary influence:</td>
<td>Sited upwind between the community and the major source area that may be affecting it:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>To assess background influence</td>
<td>Sited upwind of the community and not downwind of any major anthropogenic source area</td>
</tr>
</tbody>
</table>

The basis of the statistical method is that urban air pollution measurements are correlated either in time at the same location, or in space with other monitors in the network. Networks are optimized by examining time series correlations from long measurement records, or spatial correlations among measurements from nearby monitors. This method presupposes the existence of a monitoring network from which the time and space correlation fields can be estimated.

The basis for the modelling method is that dispersion of pollution can be predicted, to a certain extent, from knowledge of emission characteristics and the meteorological fields. Modelling results can be used to site monitors in locations that meet specific criteria such as the location of maximum concentration or the location of the most frequent exceedance of threshold values. This method requires a reasonable knowledge of the spatial variation of sources and meteorology.

NAPS Guidelines for locating monitors in an urban area identify sites as residential, commercial and industrial. In many instances, existing NAPS sites should be applicable to CWS monitoring objectives and will be designated for CWS achievement determination reporting based upon individual site assessments.
Urban PM$_{2.5}$ Locations

For urban PM$_{2.5}$ monitoring, a CWS reporting station or stations should preferably be located within the populated community area and with consideration of conditions and/or surroundings (see also Table 4) such as:

- residential or commercial locales where outdoor activities typically exist (e.g., vicinity of school, park, etc.);
- at least one centralized site in the vicinity of the populated downtown and/or suburban area;
- generally open flat area(s) with structural similarity and absence of nearby multiple high-rise buildings in at least three relevant directional quadrants;
- appropriate distances from heavy industrial activity, major arterial traffic routes and other major primary particulate emission sources.

It is recognized that such site areas may not necessarily coincide with maximum particulate concentrations within the urban area (which typically occur closer to specific emission sources), but should reflect airshed concentration ranges and temporal trends to which widespread populated areas may be exposed in conjunction with the community activities. Since even small nearby sources can inordinately affect measured levels, it is important to ensure adequate distances from localized sources.

For confirming the suitability and satisfactory positioning of an existing NAPS station, the site location and associated data should be reviewed with considerations such as:

- the existing site is located within the confines of the CMA spatial domain (based on map overlays) and in the vicinity of a major population centroid (as a means to examine the extent of any urban changes since original monitor installation);
- the site continues to meet NAPS siting criteria (to address any changes in obstructions such as new buildings or nearby tree growth);
- the site is generally downwind of urban activities based on long-term prevailing wind conditions and pollutant roses;
- the particulate concentration data are not disproportionately affected by very localized source emission rates. This can generally be assessed by determining inter-station statistical correlations, and examining the consistency of diurnal patterns and pollution roses, as well as other site data evaluations, where available (e.g., intercomparative particulate species information).

The designated site data should be, as much as possible, representative of the collective urban source particulate contributions, as well as concentrations transported into the reporting area, as opposed to reflecting emission rate influences from a single stationary source and/or a specific roadway (which could change over time). In designating sites for some areas, it may be useful to consider applying a site acceptance criterion that has been used as a screening procedure in a U.S. monitoring network (U.S. EPA 1994), but with specific modifications. For example, consideration should be given to either additional site evaluations or a site move in cases where an individual upwind local source, within a defined radius (e.g., 3 km) and predominant wind direction (e.g., 30% frequency) contributes more than 10% of the measured average PM$_{2.5}$ concentration at the existing site. Since used in a different type of application, this type of approach would require knowledge of an estimate of the local source emission rates as well as an evaluation of the numerical coefficients for the screening criterion. It must be recognized that very limited information is currently available to consider siting requirements addressing potential locally generated secondary particulate matter.

In areas where existing NAPS sites are considered by jurisdictions to be unsuitable for CWS reporting requirements and/or new sites might be desired, site selection should be done using information such as:
• finely gridded or otherwise spatially-resolved primary particulate emission inventory data for the urban area, including point source data (e.g., NPRI or other information) and estimated area, mobile and open source data (allowing for location of relevant emission sources and gridded emissions with temporal resolution, where necessary);
• projected land use information for the urban area, especially for major traffic routes;
• application of dispersion models, and/or wind rose data in conjunction with relevant long-term meteorological data, to identify a monitoring locale within a populated area that may be subject to predicted elevated daily concentrations.

As an alternative, short-term monitoring within the community could be considered for comparison of resulting data with the existing NAPS site. One approach might be to use portable particulate monitors (e.g., GRIMM or other) to determine spatial concentration patterns within the community over appropriate time intervals, achieving sufficient duration to allow for statistical comparisons. This would facilitate site selection, provided local source influences and pertinent meteorological conditions were also accounted for in the short-term monitoring design.

Similar considerations apply for ozone monitoring but at least one monitor in large metropolitan areas should be located at the representative maximum concentration locale of a CWS reporting area within the urban perimeter. Usually this location is at the downwind location of the reporting area. Wherever appropriate, ozone and PM$_{2.5}$ monitors for CWS reporting should be collocated.

**Urban Ozone Locations**

There are several factors to consider in siting ozone monitors that are intended to capture maximum urban ozone concentrations within population centres, including:

• the locations of precursor source emissions within the community that can locally generate as well as scavenge ozone;
• general directions from which transported ozone (generated from external source emissions) may enter the community;
• the prevailing morning and afternoon wind vectors for the locale in relation to source areas, especially on high temperature humid days, during both the smog and other seasons;
• the presence of a large water body bordering the urban area (over which transported ozone may tend to accumulate) in conjunction with a populated shoreline;
• highest ozone concentrations might be expected during synoptic stagnation conditions when both local and distant sources contribute to the levels.

Consideration should be given to reviewing data for the existing NAPS sites, which may be designated for CWS ozone reporting in each CMA, including aspects such as:

• wind directions, from long-term meteorological data and/or wind roses for the specific CMA areas, in relation to NO$_x$/VOC source locations and site alignment, especially for afternoon periods on days that are conducive to ozone formation. The site should be considered acceptable if located somewhat downwind of the urban sources, including the perimeters of the urban boundary, provided it also meets other relevant criteria noted below;
• examine average diurnal patterns for the site ozone concentrations to evaluate consistency and/or any abnormal features (e.g., traffic influence);
• verify the site is within populated areas of the CMA boundaries using map overlays including land use planning maps, where available;
• ensure the site continues to meet NAPS site selection criteria;
• records of NO and O$_3$ concentrations for the site with consideration of further site evaluations if ozone levels are consistently <30 ppb (i.e., as a reported indicator of local source O$_3$ scavenging such as NO titration) (U.S. EPA 1998);

• site acceptance criterion, with respect to ensuring minimized local source influences, such as that used in a U.S. photochemical air monitoring network site selection guideline (U.S. EPA, 1998). For example, further evaluations of the existing site acceptability should be considered if individual localized upwind source precursor emissions contribute greater than 10% of the measured annual average ozone concentration.

In instances where an alternative ozone station is considered necessary, site selection could consider additional information such as:

• finely gridded or otherwise spatially-resolved NO$_X$ and speciated VOC emission inventory data for the urban area with seasonal and diurnal temporal resolution;

• a compilation of identified or expected days when high ozone concentrations are either known or likely to occur in conjunction with a wind rose for afternoon hours (1:00-4:00 pm) on the high O$_3$ days. The site should then be positioned within a populated section of the reporting area which is downwind of the highest precursor emission area;

• computerized photochemical air quality modelling could also be considered, where feasible, to predict the maximum downwind ozone concentrations, but would likely require significant resources to compile both the emission and meteorological inputs;

• alternative methods could be used such as short-term O$_3$ monitoring (e.g., passive sampling and analysis) at multiple locations within the community during a series of high ozone concentration days for comparison with the existing station data (U.S. EPA, 1998).

**Separation**

Separation distances between stations are dependent on population density of the area. Stations are deployed to give the most accurate measurements representing the air quality of the area. Usually this is in the order of 6 to 8 kilometres for urban locales. Such spatial scales and separation distances are more applicable to gaseous and very fine particulate matter, which are often relatively homogenously distributed and spatially dispersed within airsheds, than some other parameters. This type of fairly uniform distribution is recognized by rationalization of sites for some components within the U.S. national ambient air monitoring strategy (U.S. EPA 2005). However, greater variability between sites often occurs for the coarser fractions of particulate matter due to the presence of more localized source impacts. This might require either middle-scale measurements or special study characterizations to accurately represent urban coarse particle distributions.

**4.4.2 Rural Networks**

**Distribution**

Regional transport/background monitoring is used to determine the upwind concentration of PM$_{2.5}$ and ozone from communities that may be significantly influenced by pollution from transboundary source regions or high background levels. Factors such as prevailing meteorology, geography and proximity to transboundary source regions will be used by jurisdictions to determine the number of upwind monitoring stations required.

**Location**
Rural monitoring sites should be located upwind of the non-compliant community in question. In addition, for assessing the transboundary influence these sites should be located between the community and the major source area that may be affecting it. For assessing the background influence, rural sites should not be downwind of any major anthropogenic source area. Analytical tools such as back trajectory models, pollution roses and modelling can be used to select the most appropriate areas for locating these monitors.

4.5 Sampling System

The proper design of the sampling system in a monitoring station is crucial. The temperature stability of the shelter, the location of the sampling probe, the design of the manifold system, the length and material of transfer lines, and the filters and fittings all affect the integrity and true representation of the air sample and the resulting data quality.

4.5.1 Shelter Requirements

Analyzers are housed inside secured buildings or shelters with restricted access to the public. The shelter must be ventilated, heated and cooled to maintain a stable temperature in the range of 20 to 30°C throughout the year. It must have good lighting and a reliable electric power supply. Telecommunication service should be available for telemetry and voice communications. An ABC class fire extinguisher and a first aid kit must be furnished in the shelter for emergency situations.

4.5.2 Probe Siting Criteria

The siting of air sample inlet probes strongly influences the quality of monitoring data. Table 5 summarizes the NAPS requirements according to the class designation of the monitoring stations and their scale of representation. Table 6 specifies the minimum distance from roadways for O₃ and NO₂ analyzers. The site criteria specified are to be followed as closely as possible to ensure uniform data collection. The following considerations apply to the siting of probes:

1. Probe height
2. Probe distance from roadways and other sources
3. Probe distance from airflow restrictions
4. Probe distance from trees

Sites must meet the criteria for probe height for each pollutant being monitored. For PM₂.₅ monitoring, the probe (sample inlet) height should be positioned within the range of 2-15 metres above ground level and in accordance with specifications, pertaining to distance from roads, indicated in Figure 2. Although actual inlets will physically differ, a similar probe height range is applicable to O₃ monitoring along with roadway distance specifications related to traffic volume. Deviations from the road distance criteria are examined individually in relation to the monitoring objectives for the site. It should be recognized, however, that for neighbourhood and urban scale of representation, all probe location criteria must be met. This requirement would include all CWS reporting sites.

Once the general station siting is selected, specific location criteria applicable to ambient air quality monitoring probes and monitoring paths need to be determined. The specific siting criteria are pollutant-specific and may vary based on the spatial scale of representativeness. Some of the key considerations in determining specific site selection include the following (Table 5).
### Table 5: NAPS Network Sample Probe Siting Criteria

<table>
<thead>
<tr>
<th>Pollutant (Scale)</th>
<th>Height Above Ground (metres)</th>
<th>Distance from Supporting Structure (metres)</th>
<th>Other Spacing Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particulate Matter: TSP, PM$<em>{10}$, PM$</em>{2.5}$ (Middle, Neighbourhood and Urban Spatial Scales)</td>
<td>2 to 15</td>
<td>&gt;2</td>
<td>a. &gt;20 m from trees</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b. Distance from the sampler to any air flow obstacle (i.e. buildings) must be &gt;2 × height of obstacle above the sampler</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c. Unrestricted air flow in 3 of the 4 wind quadrants</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>d. No nearby furnace or incineration flues</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>e. Distance of sampler from roads varies with the height of the sampler from the ground as depicted in Figure 2</td>
</tr>
<tr>
<td>Particulate Matter (Regional Scale)</td>
<td></td>
<td></td>
<td>a. 15–100 km from large city</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b. 100 m from nearest major highway (50,000 v/d)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c. 40 m from nearest traffic</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>d. 20 km from tree canopy</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>d. Avoid low-lying areas subject to drainage flows.</td>
</tr>
<tr>
<td>SO$_2$ (Middle, Neighbourhood and Urban Spatial Scales)</td>
<td>3 to 15</td>
<td>&gt;1</td>
<td>&gt;1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b. Distance from the sampler to any air flow obstacle (i.e. buildings) must be &gt;2 × height of obstacle above the sampler</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c. Unrestricted air flow in 3 of the 4 wind quadrants</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>d. No nearby furnace or incineration flues</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>e. Probe height must be &gt;0.8 of the mean height of surrounding buildings</td>
</tr>
<tr>
<td>CO (Middle Scale)</td>
<td>3 to 5</td>
<td>&gt;1</td>
<td>&gt;1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b. 2–10 m from roadway</td>
</tr>
<tr>
<td>CO (Neighbourhood and Urban Scale)</td>
<td>3 to 10</td>
<td>&gt;1</td>
<td>&gt;1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b. Unrestricted air flow in 3 of 4 wind directions</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>a. &gt;20 m from trees</td>
</tr>
</tbody>
</table>

Ambient Air Monitoring Protocol for PM$_{2.5}$ and Ozone
### Ambient Air Monitoring Protocol for PM$_{2.5}$ and Ozone

<table>
<thead>
<tr>
<th>Pollutant (Scale)</th>
<th>Height Above Ground (metres)</th>
<th>Distance from Supporting Structure (metres)</th>
<th>Other Spacing Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>O$_3$</strong> (Neighbourhood and Urban Spatial Scales)</td>
<td></td>
<td></td>
<td>b. Distance from the sampler to any air flow obstacle (i.e. buildings) must be $&gt;2 \times$ height of obstacle above the sampler</td>
</tr>
<tr>
<td><strong>O$_3$</strong> (Regional Scale)</td>
<td></td>
<td>a. 30–100 km from large city</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>b. 250 m from nearest major highway (10,000 v/d)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>c. 20 m from nearest roadway (1,000 v/d)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>d. Avoid NO$_X$ sources</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>e. Avoid low lying areas subject to drainage flows</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>f. Location on top of a small hill is desirable</td>
<td></td>
</tr>
<tr>
<td><strong>NO$_2$</strong> (Middle Scale)</td>
<td>3 to 5</td>
<td>&gt;1</td>
<td>&gt;1</td>
</tr>
<tr>
<td></td>
<td>a. &gt;20 m from trees</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>b. 10 m from street intersection or at mid-block location</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c. &gt;2–10 m from roadway</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>NO$_2$</strong> (Neighbourhood Scale)</td>
<td>3 to 15</td>
<td>&gt;1</td>
<td>&gt;1</td>
</tr>
<tr>
<td></td>
<td>a. &gt;20 m from trees</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>b. Distance from the sampler to any air flow obstacle (i.e. buildings) must be $&gt;2 \times$ height of obstacle above the sampler</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c. Unrestricted air flow in 3 of the 4 wind quadrants</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>d. Spacing from roadway varies with road traffic as specified in Table 4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**
1. When a probe is located on a rooftop, this separation distance is in reference to walls, parapets, or penthouses located on the roof.
2. Distance depends on the height of furnace or incinerator flues, type of waste or fuel burned, and quality of fuel (sulphur and ash content). This is to avoid undue influences from nearby sources.

**Horizontal and Vertical Placement of the Probe**

Criteria such as population exposure, spatial scales of representativeness, location of the supporting structure, protection from vandalism and prevailing wind direction need to be considered in determining the horizontal and vertical placement of the probe. Vertical concentration gradients of some parameters can...
occur within urban and other areas, especially for the special case of street canyons and for coarse particle size fractions (Puxbaum and Baumann 1984, Micallef and Colls 1998, Vakeva et al 1999, Chan and Kwok 2000, Watson and Chow 2000, Wu et al 2002). Studies have shown significantly higher PM$_{10}$ concentrations at breathing zone height compared to higher elevations. For CWS reporting consistency between CMA monitoring sites and between overall urban areas, it is recommended, where possible, to consider designating greater siting priority to stations with inlets at similar heights and closer to ground level than sites with elevated probe inlets.

**Figure 2: Acceptable Zone for Siting Particulate Monitors**

![Figure 2: Acceptable Zone for Siting Particulate Monitors](image)

**Spacing from Roadways**

Roadways tend to contribute to the levels of NO$_X$ and PM in the ambient air. Thus, based on the pollutant of concern and the monitoring objective, spacing from roadways needs to be determined. For example, in siting an ozone analyzer, destructive interferences from sources of NO$_X$ need to be minimized. Thus, average daily traffic is an important criterion in determining distance from the nearby roadways. Until more definitive data for PM$_{2.5}$ siting are available, it is recommended, on an interim basis, to consider using similar roadway distance/traffic volume criteria for PM$_{2.5}$ siting, as applied to O$_3$ and NO$_X$ monitoring (Table 6), along with a minimum distance of at least 25 metres from roadways. This would also facilitate collocating PM$_{2.5}$ and O$_3$ monitors.

**Spacing from Trees and Buildings**

Trees can provide surface for SO$_2$, O$_3$ or NO$_2$ adsorption or obstruct wind flow. Particulate matter can also deposit or impact on surfaces with subsequent potential releases. To reduce this possible interference, it is recommended that the probe or at least 90 percent of the monitoring path should be 20 metres away from the drip line of trees. For most other pollutants, distances greater than 10 metres from the trees are generally recommended. Buildings and other obstacles can obstruct normal wind flow around a probe or monitoring path. To avoid this possible interference, the probe or at least 90 percent of the monitoring path must have
unrestricted airflow and be located away from obstacles so that the distance from the probe or monitoring path is at least twice the height that the obstacle protrudes above the probe or monitoring path.

Table 6: Minimum Distance from Roadways for \text{O}_3 and \text{NO}_2 Analyzers

<table>
<thead>
<tr>
<th>Average Traffic (vehicles per day)</th>
<th>\leq 10,000</th>
<th>15,000</th>
<th>20,000</th>
<th>40,000</th>
<th>70,000</th>
<th>\geq 110,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum Distance between Roadway and Analyzer (metres)</td>
<td>\geq 10</td>
<td>20</td>
<td>30</td>
<td>50</td>
<td>100</td>
<td>\geq 250</td>
</tr>
</tbody>
</table>

4.5.3 Manifold Design

The design of the air sample inlet manifold is important to obtaining high-quality data. It serves to reduce the problem of moisture condensation, pressure drop and dust settlement as the air is taken from the exterior to the interior of the sampling shelter. The manifold should conserve the integrity of the pollutant concentration of the air sample as it is taken from the air mass and introduced to the inlet of the analyzers.

4.5.4 Site and Analyzer Operation

The daily operation of the monitoring site and the analyzers is the responsibility of the station operating agencies. The designated network manager is responsible for overseeing the operation of the monitoring sites by the trained operators. Operation of the site includes site visits by the operator, regularly scheduled zero and span verification, calibration, preventative maintenance and documentation. Table 7 summarizes the activities in the operation of NAPS stations.

Table 7: Summary of NAPS Station Work Activities

<table>
<thead>
<tr>
<th>Tasks in the Operation of NAPS Station</th>
<th>Work Performed By</th>
<th>Minimal Frequency for this Work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regular Site Visitation</td>
<td>Station Operator</td>
<td>Weekly</td>
</tr>
<tr>
<td>Zero and Span Verification</td>
<td>Automated</td>
<td>Weekly</td>
</tr>
<tr>
<td>Analyzer Calibration</td>
<td>Calibration Technician</td>
<td>Every 6 months; after repairs are made to the analyzer; and when an analyzer is installed at the station</td>
</tr>
<tr>
<td>Internal Performance and System Audit</td>
<td>Agency Auditor or Technician other than the operator of the station</td>
<td>Annually</td>
</tr>
<tr>
<td>External Performance and System Audit</td>
<td>Environment Canada Auditors</td>
<td>Once every 2 years</td>
</tr>
</tbody>
</table>

4.5.5 Background Siting Aspects

In some instances, CAPMoN sites and associated ozone measurement data may be applicable to CWS background concentration reporting. The CAPMoN program was established for monitoring of acid
deposition at representative background sites across Canada with addition of continuous gaseous measurements such as ozone in the late 1980’s. The monitoring sites were selected to meet the network objectives for regional-scale precipitation monitoring, to assess the chemical composition associated with distant emission sources (sometimes >1000 km from the sites) with essentially no local source contribution. In general, the stations are located in rural background and/or remote areas to represent the general topography, flow patterns and precipitation characteristics of the area. Specific CAPMoN sitting criteria, applied to avoid local source influences, are summarized in Table 8.

**Table 8: CAPMoN Station and Probe Siting Criteria**

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Sampling Height Above Ground (metres)</th>
<th>Influence</th>
<th>Spacing Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial Pollution Sources</td>
<td>3</td>
<td>&gt;50 km for individual point sources (exceeding 10,000 tonnes SO$_2$ or NO$_X$ emissions) or the sum of collective point and area sources (exceeding 10,000 tonnes SO$_2$ or NO$_X$ emissions)</td>
<td></td>
</tr>
<tr>
<td>Population Centres</td>
<td></td>
<td>&gt;5 km from small towns or villages (population &lt;5000)</td>
<td>&gt;10 km from larger towns (population 5,000-10,000)</td>
</tr>
<tr>
<td>Water Bodies</td>
<td></td>
<td>&gt;10 km from Great Lakes shoreline</td>
<td>&gt;40 km from large water body (ocean, gulf)</td>
</tr>
<tr>
<td>Transportation Routes</td>
<td></td>
<td>&gt;500 m from any roads, canals, railways (except seldom traveled access road)</td>
<td>&gt;3 km from small airports</td>
</tr>
<tr>
<td>Local Pollution Sources</td>
<td></td>
<td>&gt;500 m from small-scale pollution sources (as specified)</td>
<td></td>
</tr>
<tr>
<td>Agricultural Activity</td>
<td></td>
<td>&gt;500 m from any intensive agricultural activity</td>
<td></td>
</tr>
<tr>
<td>On-site Obstructions</td>
<td></td>
<td>Distance of the sampler from any air flow obstructions must be &gt;2.5 x height of obstacle above the sampler (e.g., trees, towers, poles, etc.)</td>
<td></td>
</tr>
<tr>
<td>On-site Buildings</td>
<td></td>
<td>Distance of the sampler from any on-site buildings must be 10X height of the building</td>
<td></td>
</tr>
</tbody>
</table>
5. DATA QUALITY OBJECTIVES

5.1 Purpose of Data Quality Objectives

Data quality objectives (DQOs) are statements that document specific data quality criteria that must be satisfied in order to have adequate confidence in the conclusions of studies based on the data. The U.S. EPA’s 1994 Photochemical Assessment Monitoring Stations (PAMS) Implementation Manual (US EPA, 1994) defines DQOs as “statements that relate the quality of (environmental) measurements to the level of uncertainty that decision makers are willing to accept for results derived from the data.”

In order to meet these requirements, the measurements must have attributes that can be expressed quantitatively and qualitatively. In the context of these guidelines, DQOs are defined as “measurable attributes of the monitoring data that will allow program objectives and measurement objectives to be met.” Table 8 summarizes the DQOs for PM$_{2.5}$, ozone and specific precursor parameters. The data quality attributes (accuracy, precision, completeness, comparability, averaging period, measurement cycle and spatial representativeness) are defined in the glossary. Spatial representativeness is covered in Section 4 of this document.

**NOTE:** Reference to Canadian documents (e.g., SOPs, reference methods) has to prevail where applicable.
5.2 Data Quality Objectives for PM$_{2.5}$ and Ozone

Ambient air monitoring networks measuring PM$_{2.5}$ and ozone to meet CWS objectives should use measurement methods that will achieve at least the minimum DQOs described in Table 9. The measurement attributes for other parameters are also included, as applicable to precursor monitoring.

Table 9: Data Quality Objectives

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Accuracy</th>
<th>Precision</th>
<th>Completeness</th>
<th>Traceability</th>
<th>Averaging Period</th>
<th>Measurement Cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_{2.5}$</td>
<td>± 20%</td>
<td>&lt;10%</td>
<td>&gt;75%</td>
<td>Reference Method$^a$</td>
<td>24 hours</td>
<td>year round</td>
</tr>
<tr>
<td>Ozone</td>
<td>± 10%</td>
<td>&lt;10%</td>
<td>&gt;75%</td>
<td>Traceable to primary standard</td>
<td>hourly</td>
<td>year round</td>
</tr>
<tr>
<td>PM$_{10-2.5}$</td>
<td>± 20%</td>
<td>&lt;10%</td>
<td>&gt;75%</td>
<td>Reference Method$^b$</td>
<td>24 hours</td>
<td>year round</td>
</tr>
<tr>
<td>CO</td>
<td>± 15%</td>
<td>&lt;10%</td>
<td>&gt;75%</td>
<td>Traceable to standard reference material</td>
<td>hourly</td>
<td>year round</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>± 15%</td>
<td>&lt;10%</td>
<td>&gt;75%</td>
<td>Traceable to standard reference material</td>
<td>hourly</td>
<td>year round</td>
</tr>
<tr>
<td>NO$_X$</td>
<td>± 15%</td>
<td>&lt;10%</td>
<td>&gt;75%</td>
<td>Traceable to standard reference material</td>
<td>hourly</td>
<td>year round</td>
</tr>
<tr>
<td>VOC</td>
<td>species dependent</td>
<td>species dependent</td>
<td>&gt;75%</td>
<td>Individual lab standard</td>
<td>24 hours</td>
<td>year round</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>Traceable to transfer standard</td>
<td>24 hours</td>
<td>year round$^c$</td>
</tr>
</tbody>
</table>

$^a$ The manual, 24-hour, gravimetric NAPS reference method. Equivalency criteria for continuous PM$_{2.5}$ mass concentration measurements in Canada are specified below. Both manual and continuous PM$_{2.5}$ monitors should be operated for CWS measurements in accordance with available Environment Canada Standard Operating Procedures (EC 2009a, b & c) and/or subsequent documents as they become available. The accuracy range refers to gravimetric or sensor accuracy without account of potential sampling artifacts.

$^b$ Reference methods for coarse particulate mass concentration have yet to be defined.

$^c$ Ammonia is monitored as part of the NAPS speciation program and is routinely measured by some NAPS agencies and at some CAPMoN sites.

NOTE: Beginning in 2011 all PM concentration data from NAPS stations will be reported at actual (local) temperature and pressure. Historically, PM has been reported at standard temperature and pressure (STP) by NAPS agencies.

It is the responsibility of individual network managers to ensure that suitable studies have been carried out to establish that newly introduced methods are able to achieve the relevant DQOs. This is particularly important for sites used to establish achievement determination (i.e., CWS Reporting Sites).

Reference materials that are traceable to national or international (e.g. NIST) standard materials should be used to establish traceability and accuracy of measurements. In the absence of Canadian reference methods, U.S. EPA Designated Reference and Equivalent Methods, or other such quality standards deemed
appropriate by the NAPS program. Adherence to these DQO measurement attributes should assist in ensuring measurement comparability.

5.3 Equivalency Criteria for Continuous PM$_{2.5}$ Instruments

As indicated in the section 6.1, continuous PM$_{2.5}$ data from intercomparison sites in Canada and elsewhere demonstrate that the use of the different commercially available continuous monitors can result in a significant variation in reported PM$_{2.5}$ mass concentrations, with location and time of year being important factors.

In the fall of 2006, the U.S. Environmental Protection Agency (EPA) amended its national air quality monitoring regulations (US FR 2006). A number of these amendments related specifically to reference and equivalent methods (specifications and test procedures) for PM$_{2.5}$ monitoring.

These regulations incorporate criteria for approval of federal equivalent methods (FEM) for manual (Class I and II) and continuous PM$_{2.5}$ (Class III), with some modifications to the method testing requirements and approval criteria. The modifications will require a more robust set of testing conditions and closer performance matching of candidate FEMs to FRMs. The criteria for PM$_{2.5}$ FEMs will facilitate the commercialization and EPA approval of continuous PM$_{2.5}$ mass monitors, allowing them to be substituted for many of the currently operating filter-based FRMs.

The testing requirements for FEMs are a vendor-driven process and the vendor must submit their application to the U.S. EPA Office of Research and Development. Minimum requirements include:

- a) Three FRM samplers and three candidate FEM samplers for each test campaign.
- b) Minimum of 23 valid sets of data per campaign (22 – 25 hours in duration for each sample).
- c) Define precision requirements for FRM and candidate FEM’s.
- d) Total of 4 sites in specifically selected geographical areas (2 winter only, 1 summer only, and California winter and summer).
- e) Criteria for multiplicative bias, additive bias, and correlation.
- f) Candidate method must “pass” at each test location (FEM tool – coming later).
- g) Data may not be transformed

The EPA has also finalized a rule for approved regional methods (ARMs) for PM$_{2.5}$. ARMs allow state agencies to optimize their PM$_{2.5}$ network with continuous methods that may not perform well in all required FEM testing regions. ARM is a monitoring agency-driven testing process that uses basically the same performance criteria as Class III methods. The testing occurs at a subset of sites in the network within which it’s intended to be used. All procedures (including use of data transformations) must be fully described in Quality Assurance Program Plan accompanying ARM application.

Limits for FEM Class III/ARM Equivalency

- Slope: 1 ± 0.1
- Intercept: -2.0 to 2.0
- Correlation Coefficient: 0.93 to 0.95 (depends on range of concentrations measured)
- Precision: < 15%
Participating NAPS agencies have agreed to adopt the acceptance limits specified for the U. S. FEM/ARM Equivalency regulation as the equivalency criteria for the continuous PM$_{2.5}$ measurements as compared with the NAPS Reference Method filter-based measurements made in Canada, as follows:

- Slope: $1 \pm 0.1$
- Intercept: -2.0 to 2.0
- Correlation Coefficient$^1$: 0.93
- Precision: < 15%

This will include the adoption of the U.S. EPA Class III FEM designated monitors$^2$ for use in Canada. That is, a vendor demonstrated that their instrument met the multiplicative bias, additive bias, correlation and precision criteria at each of the designated U.S. test sites and seasons specified. NAPS participating agencies concluded that the testing program was sufficiently rigorous as to include operating conditions found in most Canadian monitoring locations.

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$^1$ Unlike the U.S. correlation coefficient which depends on the range of concentrations measured, the NAPS correlation coefficient limit will set at 0.93 only.

$^2$ Class III FEM designated monitors require the use of a Very Sharp Cut Cyclone (VSCC) to receive an EPA designation. In Canada, Sharp Cut Cyclones (SCC) on FEM III instruments are considered acceptable, as field comparisons between the two have demonstrated no significant difference in instrument performance.
6 MEASUREMENT METHODS

Reliable monitoring of both primary pollutants and precursor constituents is essential to address CWS requirements and understand the various source-receptor relationships. Applicable measurement methods are well established for some parameters while still evolving for others. The NAPS network uses the most up-to-date available techniques which currently comprise a mix of real-time and time-integrated methods. Various potential measurement uncertainties are also recognized for each method through validity evaluations and data interpretation. While related parameters are relevant, emphasis in this section is directed toward PM$_{2.5}$ and ozone measurement techniques.

6.1 Methods for Measuring PM$_{2.5}$ Concentration

Atmospheric particulate matter is a complex mixture of solid and liquid particles that are suspended in the air. Particles that can be breathed into the lungs are known as ‘inhalable particulate’ and are smaller than 10 micrometers in aerodynamic diameter. That portion of inhalable particulate which is smaller than 2.5 micrometers is breathed more deeply into the lungs and called fine particulate (PM$_{2.5}$).

The measure of fine particulate in the atmosphere is the total mass of suspended solid and liquid particles that are less than 2.5 μm in aerodynamic diameter. These particles are comprised of carbonaceous material, sulphate, nitrate, ammonium, and other inorganic ions and trace metals.

The monitoring of PM$_{2.5}$ is challenged by the fact that a significant proportion of nitrate, ammonium and organic matter in fine particulate is semi-volatile and can result in an ‘under measure’ of actual atmospheric PM$_{2.5}$. Similarly, actual PM$_{2.5}$ may be ‘over measured’ by the presence of semi-volatile water from the atmosphere. Each type of monitor and monitor configuration affects the proportion of semi-volatile substances in the sample in its own way. Consequently, the measure of ‘actual’ atmospheric PM$_{2.5}$ is confounded by the proportion of semi-volatile particles and water in the atmosphere and by the method of measurement.

Measurements related to the reporting on achievement of PM$_{2.5}$ CWS are expressed in terms of mass concentration. For CWS achievement comparison, samples are collected for a 24-hour period on a daily basis. There are two fundamental method groups commonly used to measure the mass or mass equivalence of atmospheric PM. The first is the gravimetric method, in which particles segregated by size are collected on a pre-weighed filter medium over a specified period of time and assessed to determine PM mass. PM mass concentration is calculated by dividing the weight gain on the filter by the total volume of air (at
ambient conditions) that passed through the filter. The second group incorporates mass equivalent non-gravimetric means and includes monitors that are based on particle size distribution, optical properties, beta attenuation or inertial properties. In most instances, an engineered size-selective inlet, based on inertial separation of large and small particles, is used to fractionate the particulate matter. For most measurements, the coarse fraction is removed from the sample stream by impaction or by vortex separation using a cyclone device. During PM$_{2.5}$ monitoring, very coarse airborne particles are removed by surface plate impaction in an omni-directional PM$_{10}$ inlet device which may be followed by cyclonic removal of the remaining coarse particle size fraction (PM$_{10-2.5}$) in a sharp cut cyclone (SCC). This allows entry of only the fine particle size fraction (PM$_{2.5}$) to the collector. In some other techniques, such as the dichotomous sampler, the fine particle size fraction is separated from the coarser fraction by acceleration in a virtual impactor, in combination with differential and re-directed flow rates, to split and collect both size fractions.

Filter-based measurements of PM$_{2.5}$ in Canada using dichotomous samplers began in 1984. The ambient data used for the development of the CWS for PM$_{2.5}$ was based on this 24-hour manual gravimetric method. When the PM$_{2.5}$ CWS was signed in 2000, no reference method or performance criteria for measuring ambient PM$_{2.5}$ concentrations was specified, however, the CWS does require daily monitoring and a minimum of 75% data completeness for comparison to the Standard. Because of their lower costs of operation and their ability to provide near real-time data (required for Air Quality Indices, public air quality advisories and mapping applications), continuous PM$_{2.5}$ instruments such as the TEOM monitor and the Met-One BAM-1020 have been widely used by agencies across Canada and (elsewhere) for measuring PM$_{2.5}$. The technologies for these instruments are still evolving, however, and jurisdictions must ensure these measurements meet the equivalency criteria for reporting on achievement of the CWS.

6.1.1 Manual Methods for Measuring PM$_{2.5}$

Several PM$_{2.5}$ sampling methods are in use in Canada that allow for collection of PM$_{2.5}$ on a filter that is weighed and may be subjected to subsequent chemistry analysis. Such methods employ samplers that include dichotomous samplers, U.S. EPA Federal Reference and Equivalent Method samplers, and Interagency Monitoring of Protected Visual Environments (IMPROVE) samplers. Impaction and/or cyclonic inlets precede sample collection in order to selectively determine the particle size of interest. Specific manual methods form the basis of the NAPS Reference Method for PM$_{2.5}$ (EC, 2009a).

Manual, filter-based methods are subject to uncertainties that sometimes differ from those of continuous methods. Primary influences include variations in ambient temperature and humidity over 24-hour sample periods as well as filter handling and conditioning. Unless they are removed prior to collection on the filter, the presence of certain gases, including SO$_2$ and HNO$_3$, can increase filter weight, while evaporation of ammonium nitrate (NH$_4$NO$_3$) or semi-volatile organic compounds (SVOC) can result in weight losses. These factors are all minimized, to the extent possible, by adherence to specific quality assurance guidelines that apply to filter conditioning, sampler design, filter handling and post-sampling weighing.

NAPS PM$_{2.5}$ Reference Method (RM)

The manual, 24-hour, filter-based, gravimetric method (Method No.: 8.06/1.3/M) has been adopted as the NAPS Reference Method (RM) for PM$_{2.5}$ measurements (EC, 2009a). Standard operating procedures (SOPs) for this and other continuous PM$_{2.5}$ measurement techniques (TEOM, BAM) have been prepared. Although constituent mass loss or gain artifacts can occur during filter sampling with the NAPS RM, reference methods can provide a benchmark for comparing measurement techniques. Performance criteria for comparing continuous PM$_{2.5}$ measurements to the NAPS RM are given in the previous section (5.3).
The NAPS RM describes the operating procedures for obtaining a mass deposition on a filter from an ambient air sample with subsequent filter conditioning and gravimetric weight determination.

A particle size selective inlet (SSI) is located at the intake of a sampling tube. The inlet allows the desired size fraction of particulate matter (PM$_{2.5}$) to enter the lower portion of the flow path. The size of the particles passing through the SSI is determined by the physical configuration of the inlet and the air flow velocity. A pre-weighed Teflon filter is installed behind the selective inlet, in the lower sampler air stream where the PM is collected. After the sampling period is completed, the filter is removed and transported to a laboratory where it is weighed. The mass collected on the filter is determined by the weight difference between the filter pre-weighed mass and the after-sampling mass. The air flow of the sampler is maintained by a mechanical pump. The flow rate is controlled either by a pressure regulator and valve system or by a mass flow controller. The flow rate is measured by a mass flow meter. Using the known flow rate, the sampling time interval, and the PM mass, the volume of air sampled is calculated and subsequently the PM concentration is determined. PM concentration is expressed both in actual air volume or volume at standard conditions of 25°C and 101.3 Kpa. Data flags must be used to identify actual or reference conditions in the data set.  

**Dichotomous Samplers**

The dichotomous (dichot) sampler was the original sampler for inhalable particles. It is modelled after inertial virtual impactors in that it fractionates particles according to their aerodynamic characteristics. The dichot sampler operates at a low flow rate (16.7 L/min) relative to high volume samplers. Ambient air is drawn through an inlet head and then through a virtual impactor that separates particles into coarse (>2.5 – 10 μm) and fine (2.5 μm) fractions. This is achieved by accelerating particles through a nozzle and then drawing 90% of the flow stream off at a right angle to the flow stream, while the larger particles continue toward the collection nozzle at a reduced flow. Depending on the design, particles are collected on either 37 or 47 mm filters of inert materials (e.g., Teflon). Separation of the two size fractions minimizes potential interactions between the more acidic fine fraction and the more basic coarse fraction. However, this also requires further care in sample handling and mass determination than required with high volume size selective inlet (SSI) samples. In addition, it requires different analytical techniques than used for high volume filters (WGAQOG, 1997). In 2009, the Thermo Scientific Partisol® 2000-D Dichotomous Air Sampler and 2025-D Dichotomous Sequential Air Sampler were designated Class II FEMs by the U.S. EPA. Both of these instruments were also designated as Class II FEMs for PM$_{10:2.5}$ monitoring (US EPA, 2010).

**U.S. Federal Reference Method (FRM)**

In the United States, sampling methods for air pollution monitoring require Federal Reference Method (FRM) designation if the resultant data are to be used for measuring compliance with the NAAQS for PM$_{2.5}$.

The PM$_{2.5}$ FRM sampler was designed with two distinct engineering principles. The first is based on the exact engineering specifications that govern specific components of the monitor: the inlet, downtube, WINS (Well Impaction Ninety-Six) impactor, and filter holder specifications are identified in the U.S. Code of Federal Regulations, 40 CFR Part 50 Appendix L (US FR, 1997). The inlet was designed with 45 degree flanges to reduce the effects of inclement weather. It serves as the first “cut-point” of particles; only particles with an aerodynamic diameter of 10 microns or less are permitted into the sampling stream. The WINS impactor is the second cut-point where particles between 10 and 2.5 microns are removed from the sampling stream. Inside the impactor well, the sampling stream bends and the larger particles stick to a

---

3 Beginning in 2011, NAPS agencies will report PM in actual conditions.
filter covered with a special type of oil. The filter cassette secures the filter, preventing leaks and ensuring a proper sample. It should be noted that in NAPS manual and continuous PM$_{2.5}$ monitors, a sharp cut cyclone (SCC) is used as the second cut point, replacing the WINS impactor.

The second principle involves performance-based measurement systems (PBMS) in which manufactures adhere to a given parameter range for certain characteristics, such as operating temperature, operating pressure and flow rate, and demonstrate that their individual PM$_{2.5}$ monitors conform to those specifications. The PBMS is identified in 40 CFR Part 50 Appendix L (US FR, 1997).

Because all monitor manufacturers rely on their internal expertise to develop, design and construct PM$_{2.5}$ monitors, there is a wide range of visual and operational differences among them.

On October 17, 2006, the U.S. EPA amended its national air quality monitoring requirements (US FR, 2006) and now permits the use of an alternative second stage particle size separator in addition to the impactor-type separator (WINS impactor). The alternative separator is a cyclone-type separator Very Sharp Cut Cyclone (VSCC™).

Currently, three types of PM$_{2.5}$ gravimetric filter-based samplers adhere to criteria for FRM designation (see Table 10)

**Table 10: FRM Sampler Types**

<table>
<thead>
<tr>
<th>Type of FRM</th>
<th>Description</th>
<th>Manufacturer</th>
</tr>
</thead>
</table>
| Single-channel Sampler   | A manually operated microprocessor controlled filter-based sampler that provides one 24-hour PM$_{2.5}$ sample. | – Andersen Instruments 6/11/98
|                          |                                                                              | – BGI Incorporated 4/16/98
|                          |                                                                              | – Rupprecht & Patashnick Company 4/16/98
|                          |                                                                              | – Thermo Environmental Instruments 10/29/98     |
| Sequential Sampler       | A manually operated microprocessor controlled filter-based sampler that provides 24-hour PM$_{2.5}$ samples for multiple scheduled dates. | – Andersen Instruments 4/16/98
|                          |                                                                              | – Rupprecht & Patashnick Company 4/16/98        |
| Portable Audit Sampler   | A manually operated microprocessor controlled filter-based sampler that provides one 24-hour PM$_{2.5}$ sample. This sampler is designed to be transportable and capable of frequent sampling. The portable audit sampler is used primarily by the EPA in its national Quality Assurance Performance Evaluation Program. | – BGI Incorporated 4/6/98
|                          |                                                                              | – Andersen Instruments 3/11/99                  |
|                          |                                                                              | – Rupprecht & Patashnick Company 4/19/99        |
6.1.2 Continuous Methods for Measuring PM$_{2.5}$ Concentration

Table 11 summarizes some of the commercially available instruments currently deployed in Canada. The methods currently used most extensively in Canada include the TEOM, based on inertial properties, and the BAM-1020 beta attenuation monitor. The TEOM oscillates at a characteristic measured frequency in the absence of particulate loading on the filter. The measured decrease in frequency during operation is inversely proportional to the mass loading of particles on the TEOM filter. The BAM-1020 beta attenuation monitor employs a radioactive source ($^{14}$C) that emits a beam of high-energy electrons. As the beam passes through particulate matter deposited on the filter tape, the intensity of the beam is reduced in a manner that is exponentially proportional to mass. The availability and capabilities of commercialized real-time instrumentation for continuous measurements of particulate concentration and composition has evolved substantially in the past few years and will continue to evolve in the future.

**Tapered Element Oscillating Microbalance (TEOM™)**

The TEOM draws ambient air through a heated air inlet and an exchangeable filter that attaches to the end of a tapered quartz tube. The filtered air then passes through the hollowed tapered tube that is maintained in oscillation. An automatic flow controller directed by the system’s microprocessor maintains the sample flow at a constant rate. As PM gathers on the filter, the tube’s natural frequency of oscillation decreases. The electronics system continuously monitors this frequency, and the instrument’s microprocessor computes the total mass accumulation on the filter, as well as the mass concentrations and the mass rate, in real time.

Sample air is drawn in at a flow rate of 16.7 L/min, and a flow splitter channels a 3 L/min portion to be filtered. To standardize sampling and weighing conditions, the filter and the airstream passing through it are heated to 40°C, ensuring that the filter is always above the dew point.

In the presence of semi-volatile particulate material, volatilization from the filter surface is recognized to occur, especially when the sample stream is heated. Studies indicate that there is discrepancy between PM$_{2.5}$ measurements using the TEOM and the manually-weighed filter methods. The experimental data also indicate that the discrepancy decreases in proportion with the temperature differential between the air sample and the operating temperature of the TEOM. Temperature reduction and retrofit moisture control components have reduced but not yet resolved the volatilization losses (Schwab et al, 2004b).

A Filter Dynamic Measurement System (FDMS) version TEOM has been developed, which incorporates a cooled (4°C) filter purge stream channel that is alternated during sampling with the regular sample stream in order to automatically compensate for semi-volatile PM (SVPM) losses. This modified instrument has now been commercialized. Recent instrumental comparisons have indicated that the TEOM-FDMS provides ambient PM$_{2.5}$ concentrations with reduced or eliminated sampling artifacts relative to other commercially available continuous or manual filter-based methods (Solomon and Sioutas 2006).
<table>
<thead>
<tr>
<th>Observables</th>
<th>Methodology</th>
<th>Specification</th>
<th>US EPA FEM Status</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM&lt;sub&gt;2.5&lt;/sub&gt; or PM&lt;sub&gt;10&lt;/sub&gt; by Tapered Element Oscillating Microbalance (TEOM)</td>
<td>Particles are continuously collected on a filter mounted on the tip of a hollow glass element that oscillates in an applied electric field. The resonant frequency of the element decreases as mass accumulates on the filter, directly measuring inertial mass. System temperature is maintained at a constant value, typically 30°C or 40°C, to minimize moisture uptake and avoid fluctuations in the tapered tube’s mechanical properties.</td>
<td>Particle concentration. Precision: 2.5 μg/m³ for a 1-hour average.</td>
<td>Thermo Scientific TEOM® 1405-DF Dichotomous Ambient Particular Monitor with FDMS® (PM&lt;sub&gt;2.5&lt;/sub&gt;) June 17, 2009</td>
<td>The typical signal averaging period is 10 minutes. Volatile species can evaporate due to the heated airflow. This results in lower mass concentrations compared with gravimetric methods. An FDMS TEOM has been developed, which compensates for SVPM mass losses.</td>
</tr>
<tr>
<td>PM&lt;sub&gt;2.5&lt;/sub&gt; or PM&lt;sub&gt;10&lt;/sub&gt; by Beta Attenuation</td>
<td>Beta rays (electrons with energies in the 0.01 to 0.1 MeV range) are attenuated according to an approximate exponential (Beer’s Law) function of particulate mass when they pass through deposits on a filter tape. Filter tape samplers measure the attenuation through unexposed and exposed segments of tape. The blank-corrected attenuation readings are converted to mass concentrations.</td>
<td>Particle concentration. Precision: 5 μg/m³ for a 1-hour average.</td>
<td>Met One Instruments BAM-1020 PM&lt;sub&gt;2.5&lt;/sub&gt; Measurement System June 15, 2009</td>
<td>Averaging times can be as short as 30 minutes. Encounters interference under high relative humidity. This interference is overcome by using the smart heater technology that is now integrated to the equipment.</td>
</tr>
<tr>
<td>PM&lt;sub&gt;1&lt;/sub&gt;, PM&lt;sub&gt;2.5&lt;/sub&gt; or PM&lt;sub&gt;10&lt;/sub&gt; by Grimm Particle Monitor</td>
<td>Measures continuous ambient fine particle monitor based on the optical light scattering technology where each single particle is sized and counted.</td>
<td>Particle concentration. Precision: 3 μg/m³.</td>
<td>Grimm Technologies, Inc. Model EDM 180 PM&lt;sub&gt;2.5&lt;/sub&gt; Monitor, March 22, 2011</td>
<td></td>
</tr>
<tr>
<td>PM&lt;sub&gt;2.5&lt;/sub&gt; or PM&lt;sub&gt;10&lt;/sub&gt; by Synchronized Hybrid Ambient Real-time Particulate (SHARP) Monitor</td>
<td>A C&lt;sub&gt;14&lt;/sub&gt; beta attenuation monitor is used in combination with a fast response light scattering photometer</td>
<td>Particle concentration. Precision: 2 μg/m³ 1-hour average.</td>
<td>Thermo Scientific Model 5030 SHARP Monitor (PM2.5) June 17, 2009</td>
<td>Data cycle: 1-minute</td>
</tr>
</tbody>
</table>
Beta Attenuation Mass Monitor (BAM)

Beta Attenuation Mass (BAM) monitors measure the loss of electrons as they penetrate a filter on which particles have been deposited (Wedding and Wiegand, 1993). BAM technology has also been used to measure the liquid water content of aerosols (Speer et al., 1997).

Particles are collected on a spot of filter tape. A radioactive (beta) source emits low-energy electrons. Electrons propagating through the tape are detected on the opposite side. Their intensity is attenuated by inelastic scattering with atomic electrons, including those of the particle deposit. The beta intensity is described, to a good approximation, by the Beer-Lambert relationship (Sem and Borgos, 1976; Cooper, 1976). If the beta attenuation coefficient per aerosol mass deposited on the filter is known, a continuous measurement of aerosol mass concentration becomes possible. Movement of the filter tape is needed when the aerosol loading on the deposition spot attenuates the beta intensity at the detector to near background levels (Cooper, 1975).

Lilenfeld (1975) identifies 13 different electron-emitting isotopes with half-lives in excess of 1 year, no significant emission of gamma radiation, and energies of less than 1 MeV. Carbon-14 ($^{14}$C) sources are most commonly used. The beta attenuation coefficient depends both on beta energy and on chemical composition of the aerosol. For a $^{14}$C source and typical atmospheric aerosol, the attenuation coefficient is ~0.26 cm$^2$/mg (Macias, 1976). The dependence of the attenuation coefficient on the chemical aerosol composition (Macias, 1976; Jaklevic et al., 1981) is commonly assumed to be within measurement precision, but it may bias measurements when the composition of calibration standards differs substantially from the composition of the ambient aerosol. Measurement resolution and lower detection limit for modern instruments are on the order of a few $\mu$g/m$^3$ (Courtney et al., 1982).

Historically BAM monitors typically operated at ambient temperatures and relative humidity. While these conditions tend to preserve the integrity of volatile nitrates and organic compounds, they also favour the sampling of liquid water associated with soluble species at high humidities. Under these conditions, BAM concentrations are often larger than those of collocated filter samplers for which samples have been equilibrated at lower laboratory relative humidities prior to gravimetric analysis. Sampled air can be preceded by a diffusion dryer to remove water vapour, thereby encouraging the evaporation of liquid water associated with soluble components of suspended particles. Semi-volatile component losses, primarily during winter conditions, have also been determined with this instrument (NARSTO, 2003). More recently, smart heaters have been incorporated to these instruments which control the relative humidity of the sample stream to a selected setting. All BAM-1020 units operated in the NAPS network have smart heaters installed which were originally set at 45% relative humidity (RH) control but recently (April 2006) adjusted to control at 35% RH, following instrument comparability testing. Recent comparative US testing between TEOF-FDMS and BAM-1020 monitors indicated a measurable positive summer bias in PM$_{2.5}$ measurements with the BAM-1020 monitor containing a smart heater operated at 45% RH (Schwab et al 2006). Moisture or other gaseous adsorption on the BAM-1020 glass fibre tape was suggested as a possible cause of the bias. Instrumental revisions to improve both sensitivity and measurement ‘noise’ are being addressed by Met-One such as: changing from a glass fibre to Teflon filter tape, reducing the gap between the Beta source and detector, upgrading a photomultiplier module and extending the measurement count periods (MARAMA/NESCAUM 2005).

Grimm Particle Monitor

The Grimm continuous ambient fine particle monitors are based on the optical light scattering technology where each single particle is sized and counted. The Grimm dust monitor can simultaneously measure
particles at PM$_{10}$, PM$_{2.5}$, PM$_{1}$ and PM coarse fraction (only 3 simultaneously) and can count particle distribution in more than 30 different size channels.

The monitor takes a continuous air sample with a flow controlled pump. The particles are measured by the physical principle of orthogonal light scattering. Here particles are illuminated by a laser light and the scattered signal from the particle passing through the laser beam is collected at approximately 90° by a mirror and transferred to a recipient diode. Each signal of the diode is fed, after a corresponding reinforcement, to a pulse height analyzer then classified to size and transmitted in each size channel. These counts are converted each minute to a mass distribution from which the different PM values are derived.

The Grimm utilizes a diffusion dryer to avoid condensation during measurement. The dryer is activated when the relative humidity exceeds 70%.

**Synchronized Hybrid Ambient Real-time Particulate (SHARP) Monitor**

The SHARP monitor provides a real-time measure of the PM mass concentration using a C$_{14}$ beta attenuation monitor in combination with a fast response light scattering photometer. The monitor utilizes digital filtering to continuously calibrate the photometer using integrated beta attenuation data. The system minimizes the humidity interference and loss of volatile PM components through a combination of an Intelligent Moisture Reduction (IMR) system and frequent sample filter changes.

### 6.1.3 PM$_{2.5}$ Speciation Monitoring

Since 1984 Environment Canada has been making fine particle mass measurements at National Air Pollution Surveillance (NAPS) network sites using dichotomous samplers. The Teflon filters have been routinely analyzed for elements using energy dispersive X-ray fluorescence (EDXRF) and for anions and cations using ion chromatography (IC). The coarse fraction filters from the samplers have also been submitted to the same analytical protocols. Although this program has generated a wealth of valuable data on PM$_{2.5}$ mass and components, a complete accounting of PM components could not be made since organic and elemental carbon were not being measured and ammonium nitrate was being lost from the samples during XRF analysis. In 2002 a new program was designed to allow accurate measurement of all the important components of PM$_{2.5}$, new sampling equipment was tendered and purchased and program implementation began in 2003. All collected samples are analyzed by the Analysis and Air Quality Section (AAQS) at the Environmental Science and Technology Centre (ESTC) located in Ottawa.

A complementary program was initiated by the Measurement and Analysis Research Section (MARS) of Environment Canada using the same monitoring equipment and analytical methods. The MARS samplers are deployed at Canadian Air and Precipitation Monitoring Network (CAPMoN) sites. Sites have been chosen in both programs to allow urban-rural pairing of sites. Environment Canada regional offices have installed additional speciation monitoring sites as part of the Border Initiative program. Samples from these sites are also analyzed by AAQS. Data from the Canadian PM$_{2.5}$ speciation effort will complement data been collected in the U.S. from the EPA Speciation Trends Network (STN) and the Interagency Monitoring of Protected Visual Environments (IMPROVE) program.

**Sampling Equipment and Field Operation**

Sampling sites are equipped with Thermo Partisol-Plus 2025-D sequential dichot particulate samplers or Thermo Partisol 2000-D single event dichot samplers along with Thermal Partisol Model 2300 Speciation samplers. These units employ a similar user interface and data storage systems. The speciation sampler uses
Harvard designed Chemcomb® cartridges which employ honeycomb glass denuders and filter packs with Teflon, quartz and Nylon media.

Up to 32 fine and coarse filters (16 sampling days) can be preloaded in the sequential dichot Partisol while up to 12 Chemcomb cartridges (3 sampling days) can be preloaded in the speciation sampler. At this time, the protocol is to operate the samplers once every three days and to visit the sampling sites at least once every six days. Samples are collected over 24 hours. One fine and one coarse filter sample are collected on the dichot Partisol sampler and three Chemcomb cartridge samples are collected with the speciation sampler as described below (Table 12). Sealed Chemcomb cartridges are shipped to the field pre-configured for collection of the species of interest.

**Sample Types and Target Analytes**

A brief description of the sample media and target species is provided below.

**Table 12: Sampling Modules and Target Analyte Groups**

<table>
<thead>
<tr>
<th>Unit</th>
<th>Module Description</th>
<th>Media</th>
<th>Function/Analytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichot Partisol</td>
<td>Fine Fraction Filter</td>
<td>47 mm Teflon</td>
<td>Mass, Metals*</td>
</tr>
<tr>
<td></td>
<td>Coarse Fraction Filter</td>
<td>47 mm Teflon</td>
<td>Mass, Metals</td>
</tr>
<tr>
<td>Speciation Sampler</td>
<td>Cartridge C (4 components)</td>
<td>Sodium Carbonate Denuder</td>
<td>SO2 &amp; HNO3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Citric Acid Denuder</td>
<td>Ammonia</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Teflon Filter</td>
<td>Sulphate and other major ions</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nylon Filter</td>
<td>Inorganic and Organic Ions</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pre-fired Quartz Filter</td>
<td>Nitrate, Sulphate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Teflon Filter</td>
<td>Black carbon, Organic carbon</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pre-fired Quartz Filter</td>
<td>Mass, Metals (QA Check)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Organic carbon artifact</td>
</tr>
</tbody>
</table>

6.2 **Continuous Methods for Measuring Ozone**

Technology for monitoring ambient ozone is relatively mature. In general, ultraviolet (UV) photometry is the accepted method for field use. Commercial instruments are available that can routinely exceed the DQOs for ozone stated in this document.

The specifications for ozone and other instruments are presented in Table 13. All ozone analyzers used for ambient monitoring in Canada must have received EPA reference or equivalent method designation.

**Ultraviolet Photometry Method**

These analyzers operate using ozone’s strong absorption band (254 nm) which coincides with the emission spectrum from low-pressure mercury lamps (253.7 nm). This radiation passes through a chamber (tube) containing ambient air, and the light is absorbed by ozone present in the chamber. The amount of UV light depletion is determined by comparing it with that transmitted through a reference chamber with ozone-free air. The ozone concentration is determined using the Beer-Lambert law. The use of the mercury lamp light source is preferred to burning ethylene for the reasons stated above. The analyzers compare ozone-rich and
ozone-stripped air (using MnO$_2$) and calculate the amount of ozone present in the original sample airflow. Potential atmospheric interferents include hydrocarbons, mercury vapour, SO$_2$ and styrene.

$$O_3 + h\nu(253.7 \text{ nm}) \rightarrow O_2 + O$$

In order to ensure comparability, networks should follow NAPS protocols for monitoring ozone as described in the NAPS QA Guidelines document (EC, 2004).

**Table 13: Measurement Method and Operating Specifications of NAPS Network Analyzers**

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Measurement Method</th>
<th>Monitor Type</th>
<th>Operating Range</th>
<th>Operating Temperature</th>
<th>Minimum Detection Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone (O$_3$)</td>
<td>UV Absorption</td>
<td>Continuous Automated</td>
<td>1.0 ppm or 0.5 ppm</td>
<td>15-35°C</td>
<td>0.002 ppm</td>
</tr>
<tr>
<td>Carbon Monoxide (CO)</td>
<td>Infrared Gas Filter Correlation</td>
<td>Continuous Automated</td>
<td>50 ppm</td>
<td>15-35°C</td>
<td>0.1 ppm</td>
</tr>
<tr>
<td>Sulphur Dioxide (SO$_2$)</td>
<td>UV Fluorescence</td>
<td>Continuous Automated</td>
<td>1.0 ppm or 0.5 ppm</td>
<td>15-35°C</td>
<td>0.002 ppm</td>
</tr>
<tr>
<td>Nitrogen Oxides (NO$_X$)</td>
<td>Chemiluminescence</td>
<td>Continuous Automated</td>
<td>1.0 ppm or 0.5 ppm</td>
<td>15-35°C</td>
<td>0.002 ppm</td>
</tr>
<tr>
<td>Particulate Matter (PM$<em>{10}$, PM$</em>{2.5}$, PM$_{10-2.5}$)</td>
<td>Virtual impactors; gravimetric filters; microbalance/filter; beta radiation attenuation</td>
<td>Continuous Automated and Manual Gravimetric</td>
<td>Agency specific as per operators’ procedures</td>
<td>See NAPS QA/QC Guidelines</td>
<td>1.0 µg/m$^3$</td>
</tr>
<tr>
<td>Organic Compounds</td>
<td>Manual GC/MSD</td>
<td>Manual Canister</td>
<td>compound specific</td>
<td>15-35°C</td>
<td>0.05 µg/m$^3$</td>
</tr>
<tr>
<td>Ammonia (NH$_3$)</td>
<td>Chemiluminescence$^2$</td>
<td>Continuous Automated</td>
<td>20 ppm (various lower ranges)</td>
<td>15-35°C</td>
<td>0.001 ppm</td>
</tr>
</tbody>
</table>


2. Thermo Environmental Instruments, Specifications for Model 17C Chemiluminescent Ammonia Analyzer

### 6.3 Methods for Measuring Coarse Particulate Mass

The CWS includes a provision for reviews of the standards to be conducted for 2005 and 2010, with a report to Ministers on the findings of the PM and ozone environmental and health science including a
recommendation on a PM course fraction (PM_{10-2.5}) CWS. The 2003 Report to Ministers concluded that there is evidence of health effects due to the coarse fraction; however, the available information was not sufficient to permit a recommendation on whether or not to develop a CWS at that time. The report recommended that:

- A plan be developed and initiated by 2005 to address the information gaps for this pollutant, and
- CCME revisit the question of whether or not to develop a CWS for the coarse fraction as part of the 2010 review of the CWS for PM_{2.5} and ozone.

Monitoring of PM_{10-2.5} can be advantageously accomplished by determining the difference between collocated PM_{10} and PM_{2.5} measurements. This requires essentially the same instrumentation as used for PM_{2.5} whereby one of the two concurrent operating units contains a PM_{10} inlet in place of the other specific PM_{2.5} inlet. Depending on the type of instrumentation (continuous vs. manual), the coarse fraction may be derived for a 24-hour or shorter averaging period. Urban and other fugitive dust within the coarse particle size range typically contains non-labile constituents such as: crustal/soil components, inorganic oxides, salts, and biological debris (EC, 2001). Therefore, potential filtration artifacts that can affect fine particle components, collected by both units, should effectively cancel from the coarse determination, by difference, provided the collocated sampling units are nearly identical. Precise coarse particle size measurements by this approach have been demonstrated (CASAC, 2005), however, a possible exception might relate to the condition of acidic gas reaction with filtered alkaline dust components.

On September 27, 2006, the U.S. Environmental Protection Agency (EPA) amended its national air quality monitoring requirements, promulgating a new Federal reference method for measurement of mass concentrations of thoracic coarse particles (PM_{10-2.5}) in the atmosphere (US EPA, 2006). The FRM consists of two concurrently operated low volume samplers with one measuring PM_{10} and the other PM_{2.5}. The FRM is primarily intended to be used for approval of continuous FEMs for use in the actual network and for quality assurance of network (via collocation). Associated with the new reference method, EPA also set forth explicit tests, performance standards, and other requirements for designation of specific commercial samplers, sampler configurations, or analyzers as either FRMs or FEMs for PM_{10-2.5}, as appropriate. Six FRM and FEM instruments have been designated thus far (US EPA, 2010) To date, the Met One BAM-1020 PM-coarse monitor is the only continuous monitor to have received the US EPA designation of Class III Equivalent Method to monitor PM_{10-2.5} (June, 2009).

Direct gravimetric determinations of both PM_{2.5} and PM_{10-2.5} concentrations have also been conducted for many years, within the NAPS and other North American programs, using the dichotomous sampler. This technique allows chemical analysis to be done of the separate size fractions, though this manual method is more labour intensive than the continuous methods, requires considerable care in both handling and weighing the dual filter samples, and has no practical means to provide timely or short-term (e.g., hourly) data.

### 6.4 Methods for Measuring Sulphur Dioxide

Continuous methods of monitoring ambient sulphur dioxide have been successfully utilized in Canada since the 1950s. Ultraviolet fluorescence has generally been the accepted method for field use since the late 1970s. Many commercial instruments are available that will meet or exceed the specifications for sulphur dioxide found in Table 10 of this document.

One of the primary sources of sulphur emissions to the atmosphere is the combustion fuels which contain sulphur. These gaseous emissions are oxidized to sulphuric acid aerosols or sulphates by reactions occurring in gas phase, liquid phase, or on the surface of solids; this reaction can also occur via a
combination of all three. Oxidation may involve oxidants (e.g., H$_2$O$_2$) which are formed through photochemical processes. Sulphur dioxide can be a major contributor to ambient particulate levels (PM$_{2.5}$) as well as affect the photochemical reactions that result in ozone formation.

It is important to site monitors to avoid influences from physical obstructions and nearby sources of SO$_2$.

The operation principle for the instruments is based on the absorption of ultraviolet light by the SO$_2$ molecule. These molecules become excited after being exposed to ultraviolet light of a specific wavelength and then fluoresce with a secondary emission of light of a different wavelength as they decay to a lower energy state. This is represented by the equation below:

$$\text{SO}_2 + h\nu_1 \rightarrow \text{SO}_2^* \rightarrow \text{SO}_2 + h\nu_2$$

Ambient air is drawn into the analyzer through a particulate filter and then through a hydrocarbon removal device before entering a reaction chamber. In the chamber the SO$_2$ molecules are exposed to ultraviolet light which excites the molecules to a higher energy level. They emit light energy proportional to the sulphur dioxide concentration as they decay back to a lower energy state. A specific band pass filter only allows the wavelengths emitted by the SO$_2$ molecules to be detected by the instrument.

### 6.5 Methods for Measuring Nitrogen Oxides

The monitoring of nitrogen oxides (NO$_X$) in ambient air is similar to ozone and sulphur dioxide in that it also employs a mature technology and has been widely used since the 1970s. Chemiluminescence is generally the accepted method for field monitoring. A good number of commercially available instruments are available that meet or exceed the specifications for NO$_X$ stated in Table 10 of this document.

Continuous measurement of NO$_X$ began in the 1970s after the chemiluminescent method was promulgated and acceptable calibration procedures were developed. Widespread monitoring became important with NO$_X$ being a criteria pollutant and also a precursor to ozone and PM$_{2.5}$ formation. Generally, these instruments have relatively short cycle times providing one minute readings that are used to calculate hourly and daily averages. The location of the monitoring sites is important to avoid undue influences from physical obstructions and activities in the vicinity (e.g., nearby sources such as furnace flues and high traffic areas).

The chemiluminescent method is based on the principle that nitric oxide (NO) and ozone (O$_3$) react to produce a light emission with an intensity that is linearly proportional to the NO concentration of the air sampled. The energy generated by the reaction is measured by sensitive photo-detectors. Light emissions in the infrared range result when chemically excited NO$_2$ molecules decay to a lower energy state as represented here:

$$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 + h\nu$$

Nitrogen dioxide (NO$_2$) is first transformed into NO before it can be measured following the above reaction. NO$_2$ is converted to NO via a molybdenum converter that is heated to approximately 325°C.

Ambient air is continuously drawn into the instrument through a particulate filter and then through a switching valve. This valve directs the sample either directly to the reaction chamber (NO mode) or through a molybdenum converter (NO$_X$ mode) and then to the reaction chamber. Dry air enters the reaction chamber through a high voltage arc discharge device (ozonator). The ozonator generates ozone of sufficient concentration to ensure a complete reaction with all available NO. This reaction produces excited NO$_2$ molecules, and the resulting luminescence is measured by a photomultiplier tube. In this fashion, both NO$_X$ and NO concentrations are measured and stored in the instruments memory. An electronic subtraction of the NO from the NO$_X$ provides the NO$_2$ concentration.
6.6 Methods of Measuring Ammonia

Available methods for measuring gaseous atmospheric ammonia have not yet been fully established, and limited historical data exist. Both manual and continuous methods are available and the manual time-integrated method is used most extensively in the CAPMoN program.

Time-Integrated Method

Manual sampling methods are used for time-integrated (i.e., 24-hour or shorter) measurements of both particle-phase ammonium ion (NH$_4^+$) and gaseous ammonia (NH$_3$) by initial collection on specific substrates and subsequent chemical analyses. The procedure used in the NAPS speciation network involves collection of NH$_3$ using a citric acid coated denuder and NH$_4^+$ subsequently collected on a Teflon filter with analyses by ion chromatography following aqueous extraction. Specific care is required during preparation and handling of the reactive substrates to minimize contamination (from ambient air exposure). Such procedures are often regarded to be more laborious than the continuous measurement approach.

Continuous Method

Chemiluminescence analyzers with modifications are also being used to continuously measure NH$_3$ in addition to the NO$_X$ components discussed above. The analyzer is used in combination with an upstream thermal NH$_3$ converter module whereby nitrogen species such as NH$_3$ and NO$_2$ are transformed to NO within the initial converter and, together with the original air NO content, are detected as a total N signal. The instrument then sequentially detects NO$_X$ and the associated (NO, NO$_2$) components in the normal mode, in conjunction with NH$_3$ scrubbers on separate channels, such that NH$_3$ is recorded by the total N and NO$_X$ signal difference (i.e., signal subtraction). Each of the components (NO, NO$_2$ and NH$_3$) is then provided as output. Thermo Environmental Instruments manufactures a chemiluminescent ammonia analyzer which is currently being used in the GVRD monitoring network. Specific precautions are required to address possible measurement interferences from substances that, if present, could also transform to NO within the high temperature converter (e.g., organic nitrogenous compounds, nitric acid vapour and/or ammonium containing aerosols). The possibility of losses of NH$_3$ in sampling lines before the analyzer also requires consideration.

6.7 Methods for Measuring Carbon Monoxide

Carbon monoxide (CO) has been measured in ambient air utilizing the infrared gas filter correlation method since the 1980s. Instruments are available from various suppliers that meet or exceed the specifications listed in Table 10.

In this method, ambient air which is drawn continuously through a particulate filter to a multipass optical sample cell then exits through a temperature sensor and exhausts through a flow meter. Carbon monoxide absorbs infrared radiation (IR) at wavelengths from 4.5 to 4.9 microns. The concentration in ambient air is determined based on the principle of gas filter correlation. The analyzer generates IR radiation of known intensity and measures the amount that is transmitted through the air stream.

However, because other gases and particulates also absorb IR or interfere with the transmission of IR, the instrument utilizes a modulated gas filter wheel that is positioned between the IR source and the multiple pass optical sample cell. This wheel is rotated by a synchronized motor so that the position of the wheel is known to the instrument’s logic control system. In the first position, the wheel’s band pass filter only allows the portion of the band that CO adsorbs to enter the sample cell. All of the unabsorbed IR passes through the sample cell and is measured by a detector. The second position of the filter wheel allows all of the IR to pass through the sample cell resulting in a measure of the adsorption of CO plus all other interferences and in the third position the filter allows no IR to enter the cell (dark current). The electronics
then process the various measurements (CO, CO plus interferences, dark current and original IR source strength) to determine a CO concentration.

### 6.8 Methods for Measuring Volatile Organic Compounds

Multi-component VOC monitoring is done at NAPS sites by the canister/gas chromatography mass spectrometer detection (GC/MSD) approach using accepted standard procedures. Approximately 140 substances are analyzed. Several of these target gaseous compounds participate in atmospheric chemical reactions and some of the measured precursor species can convert through atmospheric oxidation reactions to lower volatility compounds and/or form secondary organic aerosols. Some of the target species include natural biogenic emission components that are also contributors to both ozone formation and secondary organic substances.

Twenty-four hour cumulative whole air samples are taken on a regular schedule by pumping ambient air at a constant flow rate into precleaned specially-prepared evacuated stainless steel canisters which become pressurized. Following canister shipment to the Environment Canada laboratory, a portion (i.e., aliquot) of the sample is removed/transferred to a cold trap and solid adsorber, as part of the analytical equipment, for moisture separation and component preconcentration. The sample is then released by thermal desorption to the instrument for component separation on the gas chromatographic column and individual species detection by the mass spectrometer. The compound concentrations are determined on the basis of the system’s response to known amounts of individual calibration standard compounds and the aliquot volume. Mass spectrometry is recognized to be a more definitive identification technique than several other specific detectors. Due to the variable mix of potentially reactive gas phase species within the sample, frequent system performance verification is needed in order to ensure acceptable canister cleanliness, moisture management and component recoveries, especially under dry conditions. Similarly, samples are properly stored and analyzed readily to minimize gas phase reactions that could potentially take place within the sample container over prolonged time periods.
7 QUALITY ASSURANCE REQUIREMENTS

This section describes minimum QA protocols that should be applied at all sites collecting data that will be used to support the CWS for PM and Ozone. Participating agencies may have reason to exceed the minimum requirements.

7.1 Field Procedures

Site visits, instrument calibrations and program audits are all important elements of an effective QA system. Requirements are somewhat dependent on the sampling methods employed and resources available, but each element must be present in an effective QA program.

As a minimum, participating networks should meet National Air Pollution Surveillance Network Quality Assurance and Quality Control Guidelines (EC, 2004).

Calibration and operating requirements for continuous PM$_{2.5}$ monitors are identified in the NAPS Methods for TEOM and BAM (EC, 2009b & c), and subsequent documents as identified by NAPS.

Calibration and operating requirements for filter sampling of PM$_{2.5}$ mass should be done in accordance with appropriate NAPS QA Guidelines, NAPS Standard Operating Procedures, and with other guidance as identified by NAPS.

Calibration and operating requirements for ozone and other gas monitors are identified in the NAPS QA Guidelines document and NAPS Standard Operating Procedures (EC, 2009d).

7.2 Shipping Procedures

PM$_{2.5}$ filter sampling may be carried out at certain sites in support of the CWS for PM and Ozone. As these programs are implemented, they should recognize there are quality concerns associated with blank and exposed filter shipping, and these quality issues are addressed in the NAPS reference method for PM$_{2.5}$ (EC 2009a). These measures would likely include the use of carefully designed filter holders and shipping containers, and the tracking of shipping times and temperature extremes.
7.3 Laboratory Procedures

Traceable standards, precision checks and interlaboratory comparisons are all important elements of an effective QA system. Requirements are somewhat dependent on the sampling methods employed and resources available, but each element must be present in an effective QA program.

PM$_{2.5}$ mass determination from filters should be done in central labs to ensure consistency. These labs should follow the appropriate NAPS Method (8.06/1.3/M) and any subsequent revisions for determination of PM$_{2.5}$ mass (EC 2009a).

7.4 Data Management Procedures

Data validation, data flagging and meta-data are all important elements of an effective quality system. Requirements are somewhat dependent on the sampling methods employed and resources available, but each element must be present in an effective QA program.

Data managers should strive to adopt common approaches and methods for data validation and flagging and for meta-data associated with data collected in support of the CWS for PM and Ozone.
DATA MANAGEMENT

This section describes consistent data management practices for the submission, archiving and access to data that will be used to support the CWS for PM and Ozone. The data are to be stored in local, jurisdictional databases, although duplicate and supplementary data may also reside in other databases, including the NAPS Canada-Wide Air Quality Database.

8.1 Data Format

Data managers should strive to adopt common formats and structures for PM$_{2.5}$ mass and ozone data, and associated meta-data.

8.2 Data Submission

Ambient monitoring data collected to support the objectives of the CWS for PM and Ozone, particularly at CWS Reporting sites, should be submitted for inclusion in jurisdictional databases and to the NAPS Canada-Wide Air Quality Database on the following schedule, subject to modification by the appropriate data base manager:

- PM$_{2.5}$ mass from continuous methods to be submitted annually within 6 months of end of the calendar year.
- PM$_{2.5}$ mass from manual methods to be submitted annually within 6 months of end of the calendar year.
- Ozone to be submitted annually within 6 months of end of the calendar year.

8.3 Data Access

Most ambient monitoring measurements in Canada are reported to the NAPS Canada-Wide Air Quality Database. Data may be requested by contacting Environment Canada or by contacting specific provincial/territorial/regional monitoring agencies.

Standard and specific data files are available in various computer formats from the Science and Technology Section.

For further information, please contact:

Data and Publication Coordinator
E-mail: rnspa-napsinfo@ec.gc.ca
The field of ambient air monitoring is complex, and technology is evolving rapidly. Although this Monitoring Protocol identifies national standards wherever possible, these standards may need to be supplemented from time to time with new or revised guidelines.

The NAPS participating agencies are recognized as the appropriate body to revise ambient air monitoring protocols in support of the CWS for PM and Ozone.

This document references the version of the NAPS Program’s Quality Assurance guidelines current at the time of publication (EC 2004), as well as the current versions of NAPS methods for the monitoring of ozone and PM$_{2.5}$ using various measurement technologies. It should be noted that all of these documents will require revision by Environment Canada from time to time, with opportunity for input from NAPS Program partner agencies, and that whatever versions of these documents are current at any future date will always represent the minimum quality standards and technical requirements for acquiring PM$_{2.5}$ and ozone data for CWS-reporting purposes.
## Glossary

**Accuracy**
the nearness of a measurement to an accepted value – expressed in terms of error, usually as ± percentage difference from standard value.

**Comparability**
the nearness of two different measurement systems – expressed in terms of difference, usually as ± percentage difference.

**Completeness**
the degree to which valid measurements are available for a given period – often described as the percentage of total possible measurements.

**Continuous Monitoring**
measurements of ambient conditions producing data with temporal resolution of the order of minutes.

**Data quality objectives**
statements that relate the quality of (environmental) measurements to the level of uncertainty that decision-makers are willing to accept for results derived from the data.

**Measurement cycle**
the frequency at which measurements are acquired.

**Precision**
the degree of mutual agreement among several values measured by the same systems – often expressed as the deviation from the mean in terms of the relative standard deviation (% RSD).

**Quality Assurance**
those planned and systematic actions used to assure that a measurement program can consistently produce data of a known quality.

**Quality Control**
the routine use of procedures designed to achieve and maintain a specified level of quality for a measurement.

**Spatial representativeness**
consistency of measurements with actual conditions within a prescribed geographic area.
REFERENCES


