



# **Air Quality Sensor Technologies: Ozone Literature Findings**

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# Background

**In support of the Performance Benchmarks Workshop, a literature review of relevant PM and select gas phase published research findings were investigated. This investigation included:**

- Defined regulatory requirements (US, EU, China)**
- Peer review journal and proceedings-based literature**
- Journal focus was 2007-> 2017**
- Performance characteristics were recovered and categorized**
- Primary research was conducted by Ian MacGregor and the Battelle group under an EPA-defined task order**
- The investigation was ultimately limited by resources but is considered informative but not exhaustive or comprehensive**

# Literature Specifics

- Computer-based search of key words reported ~ 20000 records pertaining to the area of interest
- Reduction in total number of titles to a resource-capable level was performed
- A total of 257 titles were graded for applicability and utility associated with performance characteristics or requirements
- The titles focused on air quality sensors because inclusion of research and regulatory-grade instrumentation would have exhausted the resources
- Each retained article was graded for information pertaining to 10 common performance attributes, then organized into 16 application types and then 4 use categories

# Key Regulatory Documents

- US Code of Federal Regulations in support of the NAAQS (FRM/FEM requirements)
- US EPA Performance Standard 18
- European Commission for Standardization (CEN) through their Air Quality Directive (2008/50/EC) and EU 2015/1480)
  - Working Group 42 directed to develop sensor-based performance classifications
    - Class 1 (Indicative measurements)
    - Class 2 (Objective estimation techniques)
    - Class 3 (research, environmental education,
- United Kingdom's MCERTS (Monitoring Certification Scheme)
- People's Republic of China (HJ 654-2013,HJ 653-2013, and GB 3095-2012)

# Application Categories

- **Air quality forecasting**
- **Air quality index (AQI) reporting**
- **Community near-source monitoring**
- **Control strategy effectiveness**
- **Data fusion**
- **Emergency response**
- **Epidemiological studies**
- **Exposure reduction (personal)**
- **Hot-spot detection**
- **Model input**
- **Model verification**
- **Process study research**
- **Public education**
- **Public outreach**
- **Source identification**
- **Supplemental monitoring**

# Performance Descriptors

- **Accuracy/uncertainty**
- **Bias/trueness**
- **Completeness**
- **Detection limit**
- **Measurement duration**
- **Measurement frequency**
- **Measurement range**
- **Precision**
- **Response time**
- **Selectivity**

Variation in use of terms, units and statistical approaches made systematic categorization difficult

# Literature by the Numbers

- Of the 257 documents, **48** contained quantitative performance information. A total of 8 contained qualitative performance info. A total of **56** documents provided the primary information shared today.
- Literature most often reported sensors being used for spatio-temporal investigations (n=40)
- Performance requirements were most often reported for **ozone (52%)** followed by NO<sub>2</sub> (46%) and then PM<sub>2.5</sub> (40%). SO<sub>2</sub> reports were extremely limited (10%)
- Of the primary 48 references, 70% adjusted for measurement artifacts, 8% intentionally retained non-adjusted data. Adjustment for the remainder (22%) was not applicable
- Treatment of erroneous data was discussed in **only 35%** of the sources



## Certification Program Requirements

<b>Program</b>	<b>U.S. EPA FRM/FEM Program</b>	<b>European Parliament and of the Council Ambient Air Quality Directive (2008/50/EC)</b>	<b>Monitoring Certification Scheme (MCERTS)</b>	<b>People's Republic of China National environmental monitoring standards</b>
<b>Organization</b>	U.S. EPA	European Committee for Standardization	Environment Agency (UK)	Chinese Ministry of Environmental Protection (MEP)
<b>Type</b>	Performance Standards Certification (instruments)	Performance Standards (instruments)	Certification (instruments)	Performance Standards Certification (instruments)
<b>Pollutants</b>	Ambient $O_3$ , $NO_2$ , $CO$ , $SO_2$ , $PM_{2.5}$ , $PM_{10}$ , and Pb	Ambient $PM_{2.5}$ , $PM_{10}$ , $O_3$ , $CO$ , $NO_2$ , $SO_2$ , and $NO_3$ ,	Ambient $PM_{2.5}$ , $PM_{10}$ , $CO$ , $NO$ , $NO_2$ , $SO_2$ , $O_3$ , benzene, and benzene-like VOCs	Ambient $PM_{2.5}$ , $PM_{10}$ , $CO$ , $NO_2$ , $SO_2$ , and $O_3$ ,





## Certification Program Requirements

<b>Program</b>	<b>U.S. EPA Performance Standard 18</b>	<b>European Committee for Standardization (CEN) Technical Committee 264 (Air Quality) Working Group 42 (Gas sensors)</b>	<b>People's Republic of China Performance Standards for Air Sensors</b>
<b>Organization</b>	U.S. EPA	European Committee for Standardization	Chinese Ministry of Environmental Protection (MEP)
<b>Type</b>	Performance Standards (instruments)	Technical Specifications (air sensors)	Performance Standards (air sensors)
<b>Pollutants</b>	Source Hydrogen Chloride (HCl)	Ambient $O_3$ , NO, $NO_2$ , CO, $SO_2$ , $O_3$ , and $CO_2$	Ambient $PM_{2.5}$ , $PM_{10}$ , CO, $NO_2$ , $SO_2$ , $O_3$ , and tTVOC



## Certification Program Requirements, Cont'd

<b>Program</b>	<b>U.S. EPA FRM/FEM Program</b>	<b>European Parliament and of the Council Ambient Air Quality Directive (2008/50/EC)</b>	<b>Monitoring Certification Scheme (MCERTS)</b>	<b>People's Republic of China National environ- mental monitoring standards</b>
<b>Applications Tiers</b>	Single Tier  Designated reference or equivalent method for use in regulatory monitoring for the NAAQS	Three Tiers  1. Fixed measurements (highest quality)  2. Indicative measurements  3. Objective estimation	Two tiers  1. Fixed measurements (highest quality)  2. Indicative measurements	Single Tier



## Certification Program Requirements, Cont'd

<b>Program</b>	<b>U.S. EPA Performance Standard 18</b>	<b>European Committee for Standardization (CEN) Technical Committee 264 (Air Quality) Working Group 42 (Gas sensors)</b>	<b>People's Republic of China Performance Standards for Air Sensors</b>
<b>Applications Tiers</b>	Single Tier  Any instrumental technology that can meet performance criteria may be used.	Three tiers  Class 1 - meets the DQOs of Air Quality Directive (2008/50/EC)  Class 2: meets DQOs of objective estimation  Class 3: no mandatory performance level	Single Tier



## Certification Program Requirements, Cont'd

<b>Program</b>	<b>U.S. EPA FRM/FEM Program</b>	<b>European Parliament and of the Council Ambient Air Quality Directive (2008/50/EC)</b>	<b>Monitoring Certification Scheme (MCERTS)</b>	<b>People's Republic of China National environmental monitoring standards</b>
<b>Test Locations</b>	Laboratory and Field	Laboratory and Field	Laboratory and Field	Field
<b>Outcomes</b>	Designated reference or equivalent method by U.S. EPA	Stamp of approval for the use of specific analyzers (in their tested configuration) in national monitoring networks	Product Conformity Certificate issued for an instrument and concentration range.	Unknown



## Certification Program Requirements, Cont'd

<b>Program</b>	<b>People's Republic of China National environmental monitoring standards</b>	<b>U.S. EPA Performance Standard 18</b>	<b>European Committee for Standardization (CEN) Technical Committee 264 (Air Quality) Working Group 42 (Gas sensors)</b>	<b>People's Republic of China Performance Standards for Air Sensors</b>
<b>Test Locations</b>	Field	Field	Laboratory and Field	Field
<b>Outcomes</b>	Unknown	Any instrumental technology that can meet performance criteria may be used	Unknown	Unknown



## U.S., European Union and Chinese Regulatory Ozone Monitoring Performance Values

Pollutant	Performance Attribute	US	EU	China
Ozone	Accuracy/ uncertainty	24-hr zero drift: $\pm 4$ ppb [1]		24-hr zero drift: $\pm 5$ ppb [5]
	Measurement range	Measurement range: 0-500 ppb [1]	Measurement range: $\leq 250$ ppb [9]	Measurement range: 0-500 ppb [5]
	Detection limit	Detection limit: 5 ppb [1]		Detection limit: $\leq 2$ ppb [5]
	Response time	Lag & Rise time: 120 sec [1]	Lag & Rise time: $\leq 180$ sec [9]	Response time: $\leq 5$ min [5]

[ ] indicates reference citation number



## Percentage of Reports of DQOs/MQOs

Pollutant	Comparison	Spatio-temporal Variation	Trend	Decision Support	Other	% All Sources
Ozone (O <sub>3</sub> )	20% (5)	72% (18)	20% (5)	20% (5)	0% (0)	52% (25)

( ) represents the number of references used in the statistic



## Frequency of Monitoring Applications

Application	Ozone (O <sub>3</sub> )
Air Quality Forecasting	8% (2)
Air Quality Index Reporting	16% (4)
Community Near-Source Monitoring	48% (12)
Control Strategy	24% (6)
Data Fusion	8% (2)
Emergency Response	8% (2)
Epidemiological Studies	28% (7)
Exposure Reduction	20% (5)
Hot Spot Detection	20% (5)
Model Input	8% (2)
Model Verification	16% (4)
Process Study Research	8% (2)
Public Education	16% (4)
Source Identification	20% (5)
Supplemental Monitoring	56% (14)
Other	12% (3)
% All Information Sources	52% (25)

( ) represents the number of references used in the statistic



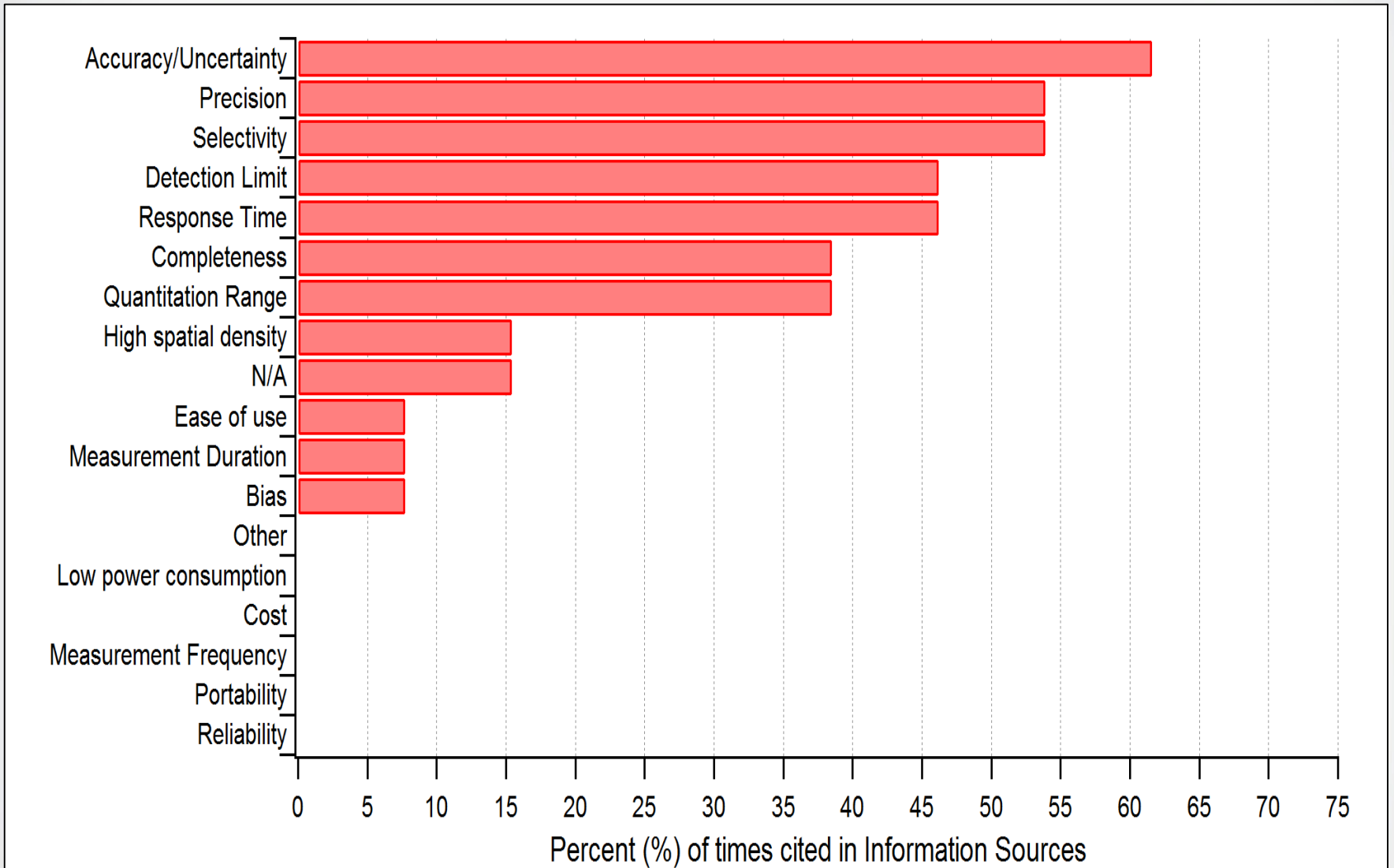


## Frequency of DQOs/DQIs Reported

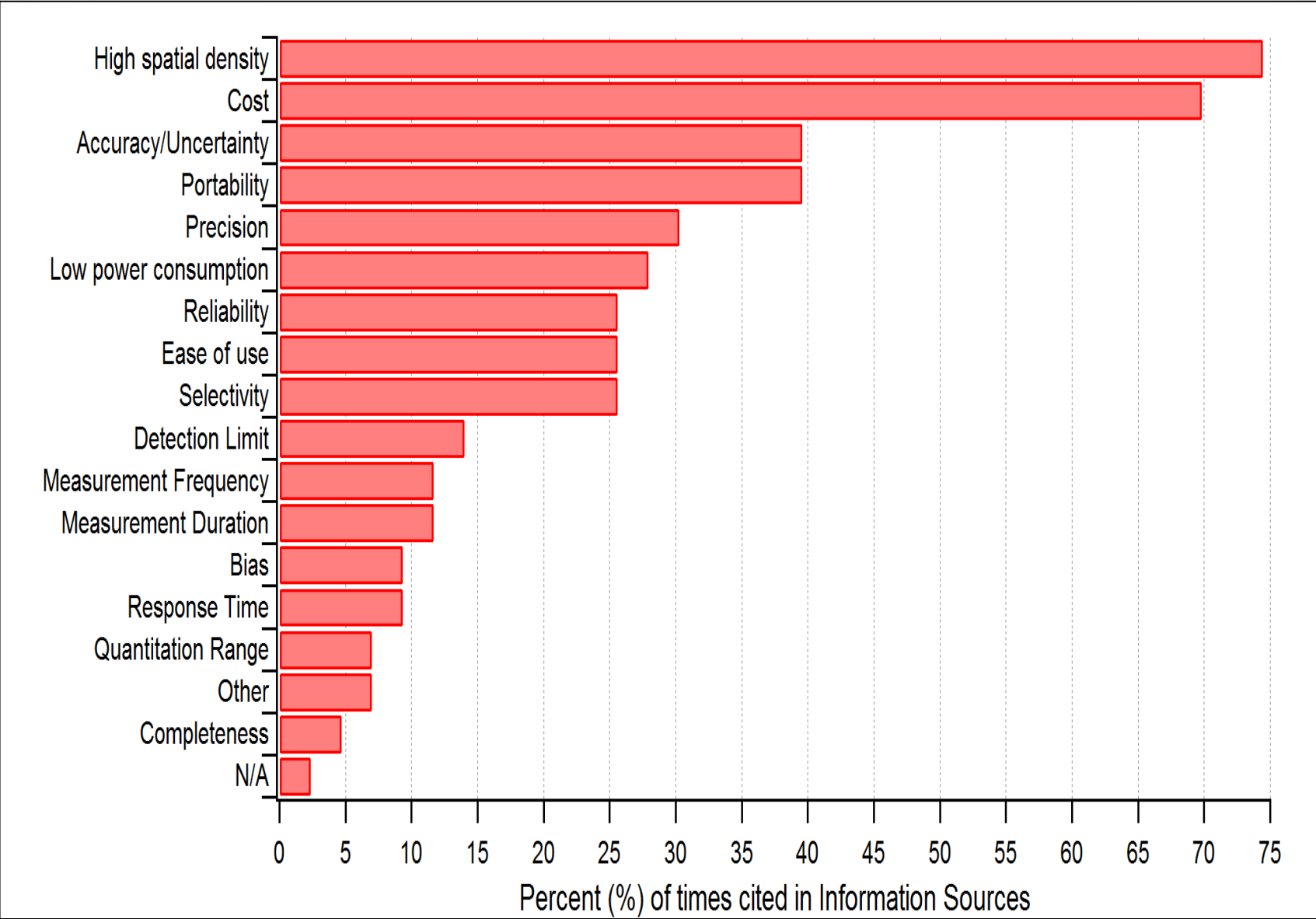
Performance Characteristic/DQI	Ozone (O <sub>3</sub> )
Accuracy/Uncertainty	76% (19)
Bias	16% (4)
Completeness	16% (4)
Detection Limit	24% (6)
Measurement Duration	20% (5)
Measurement Frequency	32% (8)
Measurement Range	40% (10)
Precision	32% (8)
Response Time	20% (5)
Selectivity	16% (4)
Other	8% (2)
<b>% All Information Sources</b>	<b>52% (25)</b>

( ) represents the number of references used in the statistic

# Decision Reporting Based References



# Non-Regulatory Use-Based References (Spatio-temporal, Comparisons, Trends)



# Sensor Comparison with Reference Monitors

**Ozone (O<sub>3</sub>)**

**$r^2 = 0.12-0.99$  (0.9)**

( ) represents median values

## Ozone DQO/DQIs and Use Category

Performance Attributes/DQIs	Spatiotemporal Variation*	Comparison	Trend	Decision Support*
<p style="text-align: center;"><b>Accuracy/ Uncertainty</b></p>	<p>Standard error (ppb): 3 [59], 5 [58]</p> <p>Estimation Error, 2<math>\sigma</math>: <math>\pm 4</math> ppb [60]</p> <p>Long-term drift: &lt;4 ppb [58]</p> <p>&lt;10 ppb/month [97]</p> <p>Short-term drift: &lt;5 ppb/24 hr [97]</p> <p>Stability over time: yearly average offset &lt; factor of 2 [91]</p>			<p>12-hr zero drift (ppb): <math>\pm 4</math> [1]</p> <p>24-hr zero drift (ppb): <math>\pm 4</math>[1], <math>\pm 5</math> [5]</p> <p>24-hr 80% span drift: <math>\pm 3.0\%</math>[1], <math>\pm 10</math> ppb [5]</p> <p>24-hr 20% span drift: <math>\pm 5</math> ppb [5]</p> <p>Long-term zero drift (ppb): <math>\pm 10</math> [5], <math>\leq 5.0</math> [9]</p>

\*U.S., EU, and China references are shown in **bold**, underline, and *italics*, respectively.

## Ozone DQO/DQIs and Use Category

Performance Attributes/DQIs	Spatiotemporal Variation*	Comparison	Trend	Decision Support*
<p style="text-align: center;"><b>Accuracy/ Uncertainty</b></p>	<p>Mean difference: 2.0 ± 1.6 ppb [58]</p> <p>Relative expanded uncertainty: 30% at 120 µg/m<sup>3</sup> over an 8 hour averaging period [84]</p> <p>R<sup>2</sup>: 0.95-0.97 [71], 0.8464-0.9801[66], (0.82-0.94, 0.8281-0.9409)[89], 0.84 [70], &gt;0.9 [67], 0.77 [64]</p> <p>Accuracy: 6.5 ppb [97]</p> <p>RMSE/σ<sub>reference</sub>: ≤ 1 [64]</p>			<p>%Diff<sub>flow</sub>: ±10% [2]</p> <p>%Diff<sub>FullScale</sub>: ±4% [5]</p> <p>Residuals of linear fit at conc. = [<u>&gt;</u>] 0 (<u>&lt;=</u> 5.0 ppb [4.0]) [9]</p> <p>Period of unattended operation: <u>3</u> months [9], ≥7 days [5]</p>

\*U.S., EU, and China references are shown in **bold**, underline, and *italics*, respectively

## Ozone DQO/DQIs and Use Category

Performance Attributes/DQIs	Spatiotemporal Variation*	Comparison*	Trend*	Decision Support*
<b>Bias</b>	Bias (%): (<20, <50) [10]	Bias (%): (<30, <30, <50) [10]	Bias (%): <50 [10]	
	Standard error (ppb): (3±2, 6) [57], (<5, 5) [58]  Mean bias (ppb): -1 [57], 0 [58]			

\*U.S., EU, and China references are shown in **bold**, underline, and *italics*, respectively

# Ozone DQO/DQIs and Use Category

Performance Attributes/DQIs	Spatiotemporal Variation*	Comparison*	Trend*	Decision Support*
<b>Completeness</b>	Completeness (%): ( $\geq 50$ , $\geq 80$ ) [10]	Completeness (%): ( $\geq 50$ , $\geq 75$ , $\geq 80$ ) [10]	Completeness (%): $\geq 50$ [10], $\geq 75$ [90]	Completeness (%): <u><math>&gt;90</math></u> [9]
	Sample frequency: $>75\%$ of available hourly data collected [92]  Time: 8 years in a 10 year period [92]			
<b>Detection Limit</b>	Detection limit (ppb): 5 [70], (1, 20) [97]			Detection limit (ppb): <b>5[1]</b> , $\leq 2$ [2]
	Resolution: 1 ppb [66]			Noise, $\sigma$ (ppb): <b>2.5[1]</b> , ( $\leq 1_{zero}$ , $\leq 5_{range}$ ) [2]

\*U.S., EU, and China references are shown in **bold**, underline, and *italics*, respectively



# Ozone DQO/DQIs and Use Category

Performance Attributes/DQIs	Spatiotemporal Variation*	Comparison*	Trend*	Decision Support*
<b>Measurement Duration</b>	Measurement duration: 1 min [60], 1 min [71], 1 min [66]		1-hr daily maximum values averaged quarterly [86]	
<b>Measurement Frequency</b>	Sample time: 10 s [88], 1 min [59], (1 min, 1 min) [88], 1 min [57], 1 min [58], hourly [89], 5 minutes [70], 5 min [55], 30 min [94]  Averaging time: >4 times the sensor response time [84]	Sample Time: (10 s, 1 min, 1 min) [88]	Sample Time: (10 s, 1 min, 1 min) [88]	
<b>Measurement Range</b>	Measurement range (ppb): (2-10000, 10-250, 0-500, 0-150, 10-1000) [88], 0-100 ppb [60], 0-150 [66], (0-250, 0-500) [97]	Measurement range (ppb): (2-10000, 0-500, 0-150) [88]	Measurement range (ppb): (2-10000, 10-250, 0-500, 0-150, 10-1000) [88]	Measurement range (ppb): <b>0-500</b> [1], 0-500 [5], ≤250 [9]

\*U.S., EU, and China references are shown in **bold**, underline, and *italics*, respectively

# Ozone DQO/DQIs and Use Category

Performance Attributes/ DQIs	Spatiotemporal Variation*	Comparison*	Trend*	Decision Support*
<b>Precision</b>	Precision (ppb): (0.5, 0.6, 2.0, 5.0, 6.0, 10, 10.3) [88]	Precision (ppb): (2.0, 5.0, 6.0) [88]	Precision (ppb): (2.0, 5.0, 6.0, 10, 10.3) [88]	
	CV: (<20%, <50%) [10]	CV: (<30%, <30%, <50%) [10]	CV: <50% [10]	
	Precision: 4% at 95% confidence level [59]  Mean absolute deviation: 1.3 [0.6-3.1] ppb [66]  $R^2 = 0.9 \pm 0.06$ [67], 0.9995 [70]			$\sigma_{20\%URL}$ : <b>2%</b> [1], $\leq 5$ ppb [5] $\sigma_{80\%URL}$ : <b>2%</b> [1], $\leq 10$ ppb [5]  Repeatability standard deviation at zero [concentration] ( $\leq 1.0$ [3.0] ppb) [9]  $\sigma$ : ( $\leq 5.0\%$ of 3-month avg) [9]  $\%Diff_{SampleCalibrationPort}$ : $\leq 1.0\%$ [9], $\pm 1\%$ [5]

\*U.S., EU, and China references are shown in **bold**, underline, and *italics*, respectively

## Ozone DQO/DQIs and Use Category

Performance Attributes/ DQIs	Spatiotemporal Variation*	Comparison*	Trend*	Decision Support*
<p><b>Response Time</b></p>	<p>Response time: 65 sec [97]</p>			<p>Response time: <math>\leq 5</math> min [5]                      Lag time (sec): <b>120</b> [1]                      Rise time (sec): <b>120</b>[1], <u><math>\leq 180</math></u> [9]                      Fall time (sec): <b>120</b>[1], <u><math>\leq 180</math></u> [9]                      Difference in rise and fall time: <u><math>\leq 10</math></u> sec [9]                      Residence time inside analyzer: <u><math>\leq 3.0</math></u> sec [9]</p>

\*U.S., EU, and China references are shown in **bold**, underline, and *italics*, respectively

# Ozone- Key Findings on Performance Attributes

## Ozone ( $O_3$ )

- Precision – no pattern present
- Accuracy/uncertainty – inconsistent information
- Response time – faster response times are needed for non-regulatory purposes such as spatiotemporal trends monitoring; note that data are limited (one spatiotemporal study, three regulatory monitoring methods)
- Measurement duration – spatiotemporal variations requires shorter measurement durations as compared to longer-term trends monitoring, in accord with expectations

# Ozone- Key Findings on Performance Attributes

## Ozone (O<sub>3</sub>)

- Measurement frequency – similar across comparison, spatiotemporal, and trends monitoring applications
- Measurement range – higher measurement ranges are required for non-regulatory air monitoring work (all but decision support-related applications)
- Completeness – requirements are most stringent for air monitoring for decision support