

**Comments on Monitoring Options for Secondary NAAQS**  
**Submitted to CASAC's Air Monitoring and Methods Subcommittee (AMMS)**  
**February 16, 2011**

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Partial funding for preparation of these comments has been provided by the American Petroleum Institute.

*A. EPA's first "Charge Question" to the AMMS is in two parts and regards both the use of the CASTNet Filter Pack (FP) to provide annual particulate sulfate data in support of the secondary NOx/SOx National Ambient Air Quality Standard (standard) as well as adoption (after development and documentation) of that method as the Reference Method for particulate sulfate.*

**Comment:** Filter-based methods such as the CASTNet FP have historically been subject to problems. This is evidenced by the artifact formation on fiberglass TSP filters in the 1970s' and the more recent 1998 problem with CASTNet filter clogging due to "inadvertent" changes in manufacturing specifications<sup>1</sup> in nylon filters. These issues point out the need for strict control of filter media specifications and for the need to test filters used in the proposed NOx/SOx secondary standard method on an ongoing basis. If this method is to be designated as a "Reference Method" the long-term physical characteristics of the filters employed must be well characterized and tracked.

Also, EPA requested comment on the stated intent to "... document the capability of the CASTNet FP to develop that method as the FRM for 'particulate sulfate' based on the existing information and procedures..." for that method. This proposed approach would include laboratory-based studies regarding filter efficiency, artifact formation, laboratory-based biases and other random bias issues.

However, the AMMS should note that not all sampling bias issues can be readily identified by either laboratory or field sampling protocols. It is of note that State-level monitoring agencies<sup>2</sup> were the first to report anomalous "crystallization" of oil in the "WINS 96" impactors that were utilized in the first phase of the EPA's "PM<sub>2.5</sub>" monitoring program. That crystallization could plausibly have affected monitoring results and a subsequent EPA report<sup>3</sup> on this topic noted that experimental conditions utilizing temperatures of -25<sup>0</sup>C. were required to "crystallize" the impactor oil while a follow-up field test indicated that crystallization occurred at ambient temperatures of only -5<sup>0</sup>C. and that crystallization was not reversed until temperatures rose to well above 0<sup>0</sup>C.

These disparate results demonstrate that ambient sampling issues exist that cannot be easily resolved by either laboratory- or field-based studies and EPA should not rely solely on either approach when considering a Reference Method. EPA should however employ empirical tests of

CASTNet FP results from monitoring sites exhibiting extreme temperature or absolute humidity conditions before adopting the CASTNet method as “Reference” for any parameter.

Finally, collocation of samplers in order to more fully characterize precision of particle sulfate data is desirable and should be pursued in the CASTNet program. However, the “...slowly changing errors that are neither random nor fixed...” noted in long-term CASTNet particle sulfate data<sup>4</sup> must be resolved before even this approach can be viewed with confidence.

***B. EPA’s second “Charge Question” to the AMMS is essentially the same as the first Charge except the parameter of interest is sulfur dioxide gas.***

**Comment:** Although there can be advantages in collecting multiple parameters from the same sampling platform, the CASTNet FP is not as robust a method as the existing UVF Reference method (noted below) and it should not be designated as a FRM for sulfur dioxide gas. However, if EPA believes the FP method can meet existing requirements for “equivalent” methods it should be submitted for such testing.

***C. EPA’s third Charge Question inquires about the use of the existing Ultraviolet Fluorescence (UVF) monitor to generate annual average SO<sub>2</sub> concentration data.***

**Comment:** As noted in comments on the second Charge Question, the UVF technique is a robust and proven method and it should be the source of annual SO<sub>2</sub> data for the proposed secondary standard.

***D. EPA’s fourth “Charge Question “ to the AMMS is in two parts and regards both the use of the existing NO<sub>y</sub> method to provide annual average data in support of the secondary NO<sub>x</sub>/SO<sub>x</sub> standard as well as adoption (after assessment and additional development) of that method as a Reference Method.***

**Comment:** The AMMS members are no doubt aware of the issues and shortcomings of existing NO<sub>y</sub> monitoring technique which might prevent/limit its applicability as a FRM. If possible, a technique that reports both NO<sub>2</sub> and NO<sub>y</sub> would be preferable to a single NO<sub>y</sub> method. This two-parameter approach could then serve the criteria pollutant primary NO<sub>2</sub> program by directly providing NO<sub>2</sub> data and as well as the NO<sub>x</sub>/SO<sub>x</sub> secondary standard program by providing NO<sub>y</sub> data.

Also, the EPA has proposed to utilize a single site (at its facilities in North Carolina) for purposes of comparing real-world, ambient operation of candidate NO<sub>y</sub> monitors. Although that approach is economical it ignores the range of meteorological conditions that exist throughout the range of “NO<sub>x</sub>/SO<sub>x</sub> Eco-Regions” noted in EPA’s Rural Network Plan<sup>5</sup>. The proposed approach ignores the potential impact of inorganic nitrates in coastal Northeastern regions, cold (sub-zero) temperatures in Northern regions, arid conditions in Western regions and high humidity in Northwestern regions.

The extremes of temperature, humidity and atmospheric composition have all historically been noted as having biased sensors, monitors and sampling systems in various monitoring programs. These real-world variables should not be ignored and EPA should expand its ambient testing to

include the most relevant of these variables. For example, EPA must address the sample chamber quenching due to water vapor in the NOy technique<sup>6</sup>.

*E. EPA's fifth Challenge Question centered on the use of data from the emerging AMoN network to evaluate Air Quality Modeling behavior with respect to characterizing ambient patterns of ammonia.*

**Comment:** Measurement of ammonia is very limited or nonexistent in Eco-sensitive Regions but is projected by some models to account for up to 30% of total nitrogen deposition in some of those regions<sup>7</sup>. Some form of ammonia measurement is needed and the AMoN network might provide a reasonable starting point. Although AMoN (passive) samplers collect 14 day samples<sup>8</sup>, this frequency may provide enough data for the "pattern" analysis stated in the Charge Question. EPA should require sufficient collocated AMoN samplers to insure that the precision of the method is adequately characterized for the intended use.

*F. EPA's sixth Challenge Question requests views on the utility of collocating AMoN samplers at each site measuring data to be used in evaluating the NOx/SOx secondary standard.*

**Comment:** In addition to method precision, collocating AMoN samplers at all NOx/SOx sites will help identify emerging or ongoing bias and imprecision associated with that method. If the AMoN approach is to be used, EPA should require collocated AMoN samplers at all sites contributing data for use in determining the secondary NOx/SOx standard.

*G. The eighth Challenge Question requests comment on the concept of locating a suite of NOy species measurements at 2-5 locations in different atmospheric and ecological regions in order to evaluate air quality model and NOy instrument behavior.*

**Comment:** As noted in the comments to item "D" above, the meteorology in the various Sensitive Eco-Regions is varied and extremes in temperature or humidity may bias some sampling methods. Atmospheric composition may also exhibit extreme differences between these regions. Therefore any additional measurements that can be made to characterize precision and bias in this extremely complex secondary standard proposal would be helpful. EPA should strive to directly measure NOy species at at least two sites in each Sensitive Eco-Region.

*H. The ninth Charge Question requests feedback on the concept of utilizing existing CASTNet and rural NCore sites as the starting infrastructure to support the NOx/SOx standard.*

**Comment:** There is merit in the suggested approach but many questions are unanswered (and perhaps unanswerable) at this time. Many of the previous Charge Questions center on extensive and yet-to-be-performed research/analysis/assessment of the capabilities of the CASTNet FP and the emerging continuous methods for NOy and/or NO2/NOy. Until results of the proposed investigations are completed only conditional support for this proposal can be given.

Additional consideration must be given to the fact that coverage of the proposed networks in Sensitive Eco-Regions in the upper midwest and northwest are extremely limited. Obviously additional sites could be situated in these areas but before that is done a thorough investigation of the value of all CASTNet/NCore sites should be performed to insure that the proper parameters are being measured at the appropriate sites in support of mandated standards.

*I. The eleventh Charge Question involves consideration of using CASTNet/NCORE sites as the “framework” for rural monitoring in the U.S. in support of both “secondary standards and evaluating the behavior of regional air quality models”.*

**Comments:** This question is essentially the same as the ninth Charge Question but adds the concept of “...evaluating the behavior of regional air quality models...” That is a critical addition because the secondary standard will not be computed by a simple averaging of data values from a network of monitors but rather will use those values as input to an air quality model. The model results will then be used by States and Tribal areas to infer their status with respect to the proposed secondary standard.

The onus of “non-attainment” of any secondary NO<sub>x</sub>/SO<sub>x</sub> standard will be borne by State/Tribal decision-makers who have traditionally used data from their own monitoring networks for such decisions. However, with this proposed secondary standard, those decision-makers will be forced to rely on “contractor-supplied” data (i.e., CASTNet) which is then filtered through air quality models which they may not have ready capacity to operate.

Thus, although the combination of data from the CASTNet/NCORE sites may be sufficient to begin formulating attainment status with respect to the to-be-proposed secondary standard – EPA must be prepared to thoroughly explain uncertainty in that data and defend its use in requiring States and Tribal authorities to expend the millions of dollars required to develop and implement attainment strategies.

## References

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