3/16/11 Draft

The Honorable Lisa P. Jackson
Administrator
U.S. Environmental Protection Agency
1200 Pennsylvania Avenue, NW
Washington, DC 20460

Subject: Review of EPA Draft Documents on Monitoring and Methods for Oxides of Nitrogen (NO_x) and Sulfur (SO_x)

Dear Administrator Jackson:

The Clean Air Scientific Advisory Committee (CASAC) Air Monitoring and Methods Subcommittee (AMMS) augmented with Members of CASAC Oxides of Nitrogen (NO_x) and Sulfur (SO_x) Welfare Panel met on February 16, 2011 to review EPA's draft documents on monitoring and methods for NO_x and SO_x. This letter provides CASAC's overall comments and evaluation. The CASAC and Panel membership is listed in Enclosure A. The Panel's responses to EPA's charge questions are presented in Enclosure B. Finally, Enclosure C is a compilation of individual panel member comments. This letter provides our consensus views on monitoring methods pertaining to EPA's consideration of proposed NO_x and SO_x Secondary National Ambient Air Quality Standards (NAAQS).

EPA has developed a novel index that integrates the potential acidifying effects from the deposition of oxides of sulfur and nitrogen called the Aquatic Acidification Index (AAI). Application of this index would no longer be based solely on NO_2 and SO_2, which historically have been used as the ambient air indicators associated with oxides of nitrogen and sulfur. Instead, the AAI would use NO_y (i.e., total reactive nitrogen including NO, NO_2, HNO_3, and several reactive organic nitrogen compounds such as n-propyl nitrate), SO_2 and particulate sulfate as the ambient air indicators. The CASAC NO_x / SO_x Welfare Panel has endorsed the use of NO_y, SO_2 and particulate sulfate as appropriate ambient air indicators, and deferred advice to EPA on the monitoring methodology and network design issues that would be used to measure these indicators to the CASAC AMMS.

Within this letter, CASAC responds to eleven charge questions associated with issues involving the measurement of various indicator compounds that would support EPA in developing a new secondary standard for oxides of nitrogen and sulfur. The CASAC AMMS Panel reviewed the following five documents that summarize various NO_x and SO_x monitoring method and network design issues:

1) "Ambient Air Monitoring For A New Secondary NAAQS For 2 Oxides of Nitrogen and Sulfur;"

2) "Characterizing Emissions, Air Quality, Deposition and Water Quality;"
3) "Air Quality Observation Systems in the United States - Draft Report;"
4) "Ambient Air Monitoring Networks Supporting Secondary Standards and Air Quality Model Improvement;" and
5) "Federal Reference Methods for NOy and p-SO4 for the New Combined NOx and SOx Secondary NAAQS - Research Plan - January 20, 2011."

Overall, CASAC believes that EPA's proposed specific methods for measuring NO_y, SO_2 and particulate sulfate ambient air indicators are suitable approaches. CASAC provides recommendations for improving the application of each method, and suggestions for lessening the uncertainties associated with such applications. CASAC agrees that EPA's proposed use of existing CASTNET and rural NCore networks as a starting infrastructure and as a framework for national rural secondary SO_x/NO_x monitoring would appropriately support attainment decisions and model evaluation if the networks are designed and located appropriately.

CASAC supports the use of the AMoN passive sampling ammonia monitoring network for model evaluation and to provide improved spatial characterization of ambient ammonia concentrations. Integrated ammonia and ammonium measurements using impregnated filters may be an ideal approach, and recommends that additional performance evaluations of the passive samplers used in the AMoN occur to make maximum use of these emerging data.

CASAC agrees it would be useful to co-locate ammonia measurements at each location where NO_y and SO_x indictors are measured, since that monitoring information would strengthen the setting of F2 values (which represent acidifying deposition associated with reduced forms of nitrogen in the AAI). EPA should gather integrated measurements at as many sites as possible in order to supplement the modeling with the measurement data and provide a greater degree of reliability in the F2 values.

CASAC also views the addition of limited NO_y speciation measurements as critical to support the proposed secondary standard in the context of validating CMAQ predictions of NO_y species, evaluation of model estimates of the transference ratios from NO_y to deposition, and understanding NO_y measurements and potential measurement biases in network deployment. Existing measurement instruments and technologies are available for necessary speciation, and EPA should consider measuring the size distribution of nitrate and also measuring other ions associated with nitrate.

Finally, CASAC notes that a missing component of the monitoring program is a measurement of water quality. Some regions of the country have relatively little water quality data in comparison to other regions. Data indicating a change in the physical ecological indicator of Acid Neutralizing Capacity (ANC) over time will provide the necessary accountability for the modeling and monitoring approach used for the secondary standard and will also provide a demonstration to the public and other stakeholders that the program is providing tangible results.

In closing, CASAC appreciates the opportunity to provide input to EPA at this stage in the process, and trusts that our comments will be useful to EPA as it revises its NO_x and SO_x monitoring methodology and addresses the network design issues.

Sincerely,

Dr. Armistead (Ted) Russell, Chair
CASAC Oxides of Nitrogen and Sulfur Oxides
Secondary NAAQS Review Panel

Dr. Jonathan M. Samet, Chair
Clean Air Scientific Advisory Committee

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Enclosure A – Roster

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Enclosure B
CASAC Air Monitoring and Methods Subcommittee (AMMS) Consensus Responses to Charge Questions

Charge Question 1: *What are the Panel's views on using the CASTNET filter pack (FP) to measure particulate sulfate for the purpose of providing annual average values as an indicator for the NOx/SOx standard? Given EPA plans primarily to document the capability of the CASTNET FP and develop the FRM for particulate sulfate based on the existing information and procedures, what are the Panel's views of this approach for setting the FRM?*

CASAC generally supports the use of the CASTNET filter pack (CFP) as a potential Federal Reference Method (FRM) for measuring particulate sulfate for this secondary SO_x / NO_x standard. The method has been relatively well-characterized and evaluated, and has a documented long-term track record of successful use in a field network designed to assess spatial patterns and long-term trends. Because the CASTNET network plays an important role in tracking Clean Air Act (CAA)-related air quality changes over space and time, the more detailed scrutiny and documentation that would result from FRM development would add confidence in the quality of CASTNET data for its many various applications.

A major advantage of specifying the CFP for particulate sulfate is to maintain the possibility that the CFP might possibly be used to supply all the measurements required to implement this NAAQS, assuming that a Federal Equivalent Method (FEM) could be specified for CFP SO_2 and that "total nitrate" (and an associated deposition transfer ratio) could be used as a surrogate for NO_y in the AAI equation. The resulting network might employ a mix of weekly filter-based and continuous methods, and address the multiple objectives of compliance determination, model evaluation and improvement, and more complete atmospheric characterization – without the need to do everything everywhere.

The time resolution of the CFP weekly data is adequate for partially determining compliance with a NAAQS with a 3 to 5-year averaging time, and sampling all the time will reduce the inter-annual variability introduced by intermittent (1 in 3 day) daily sampling in programs such as IMPROVE and CSN. Weekly time resolution is minimally useful for model evaluation and refinement, and for that objective, it would be highly desirable to consider deployment of continuous sulfate analyzers at a few sites where continuous SO_2 is being measured.

The open-faced CFP sampler would capture some coarse-phase sulfate particles that have substantially larger dry deposition velocities than their more abundant fine particle counterparts. It would be useful to see a more detailed assessment of the CFP particle cut size characteristics, as well as an analysis of the temporal and regional variations in sulfate particle size distributions.

It is not likely however that inclusion of some coarse particle sulfate in the SO_x indicator will improve (or harm) the quality of that indicator for use, in combination with an associated CMAQ deposition transfer ratio, as a predictor of total wet and dry sulfur deposition. It is also not likely that inclusion of coarse sulfate, without some specification of the particle size distribution, will provide more useful information for model evaluation than that provided by more widely deployed fine particle sulfate measurements, such as those that might be provided by IMPROVE. Conceivably, the fine particle sulfate data from larger networks like IMPROVE (in its current configuration or with enhanced filter pack supplements for other species) might be used in a complementary way to improve the spatial resolution for several of the measured + modeled S and N species.

Charge Question 2: *What are the Panel's views on using the CASTNET filter pack (FP) to measure sulfur dioxide gas for the purpose of providing annual average values as an indicator for the NOx/SOx standard? If EPA would document the capability of the CASTNET FP and develops an FRM for sulfur dioxide gas based on the existing information and procedures, what is the Panel's view of this approach for setting the FRM?*

In principle, CASAC felt that the CASTNET filter pack and other filter pack based approaches are adequate for measuring long term average SO_2 gas concentrations in rural areas with low levels (less than 5 ppbv) and therefore suitable for consideration as an FRM for the new NO_x / SO_x standard. Although FP-based approaches are widely deployed and well established, members of the Panel raised a number of concerns about the performance of FP approaches that need to be addressed: negative biases associated with alkaline soil, retention of SO_2 on the combination of nylon and impregnated filters (especially at higher flow rates), effect of relative humidity (RH) on SO_2 retention, and effects of wet filters on SO_2 retention (which is especially a concern with the CASTNET open face design). There is also a need to evaluate the CASTNET approach against the existing SO_2 FRM, focusing on weekly or longer average at low concentration rural sites. Only limited performance data on the performance of the CASTNET FP was provided to the Panel; it was not clear to the Panel that their concerns could be adequately addressed using existing information. Therefore, some additional characterization of the CASTNET FP may be needed. If EPA thoroughly documents the capability of the CASTNET FP and develops a suitable set of operating procedures, CASAC feels that the CASTNET FP would be a reasonable approach for measuring annual average values as the SO_2 gas indicator for the NO_x / SO_x standard.

Regarding model performance, the low time resolution FP data will be of limited use for model evaluation. CASAC is also concerned about inferring deposition rates from long term average concentrations because of the importance of diurnal variations in determining dry deposition, especially given the problems that models have in reproducing diurnal SO_2 profiles. During implementation, EPA will provide States with transference ratios that relate ambient concentrations of SO_x to wet and dry deposition of sulfur oxides, and the primary concern is to

obtain accurate measurements of SO_2 and SO_4. In the end, the issue is to evaluate how well models can simulate accurate transference ratios CASAC suggests two ways to address this problem. One is to continue to improve and evaluate the models to the point where there is general confidence in model capabilities; this would be essential if EPA chooses a long-term averaging approach. The second is to make high-time resolved measurements. The latter is somewhat outside the scope that EPA is considering.

Finally, CASAC emphasizes the importance of site selection and site characterization (e.g., fetch, height of inlet, height of canopy). For example, monitoring sites with poor fetch may be subject to significant concentration biases, due to localized deposition of reactive gases (primarily HNO_3 and SO_2). Such biases would likely lead to under-estimation of deposition rates and inhibit interpolation or extrapolation of deposition fields within or between sensitive ecoregions.

Charge Question 3: *What are the Panel's views on using the current primary FRM (high time resolution UVF) to measure sulfur dioxide gas for the purpose of providing annual average values as an indicator for the NOx/SOx standard?*

CASAC believes that continuous, high-sensitivity measurements of sulfur dioxide gas in representative field sampling locations would be desirable for purposes of validating both CASTNET FP measurements of sulfur dioxide and models used to calculate temporal and spatial distributions of sulfur dioxide. However, as documented in 75 FR 35597- 35601 (22 June 2010), the ultraviolet fluorescence (UVF) -FRM must meet the following performance requirements: a detection limit of 1 part per billion by volume (ppbv); maximum interference less than ±5 ppbv SO_2 equivalent; and 12- and 24-hour zero drift less than ±5 ppbv SO_2 equivalent. In the context of annual average mixing ratios of interest for the secondary standard - on the order of 1ppbv - these specifications are inadequate. Current UVF FRM sulfur dioxide monitors are, in principle, sufficiently accurate and sensitive to carry out measurements at the levels that would be required, but additional precautions would be required. For example, current procedures lead to zero offsets in the range of about 200 ppt. The use of better quality zero air would reduce the zero offset by about an order of magnitude.

Charge Question 4: *What are the panel's views on using existing NO_y methods that are deployed, for example, in NCore as the measurement approach for NO_y for the purpose of providing annual average values as an indicator for the NOx/SOx standard? What are the panel's views on EPA's assessment that additional study is needed before establishing an FRM based on the existing NO_y methods? That is, are the methods already adequately demonstrated as a reference method to determine compliance with a NAAQS? What are the panel's views on the research plan for establishing existing NO_y methods as an FRM? [Note suggested*

improvement to the plan would be appreciated, particularly ones that would help complete the study on time.]

The consensus of the Panel is that the existing NO_y method is generally an appropriate approach for the indicator. Given the large uncertainties in values associated with determining factors in the AAI , the uncertainties in the measurements are relatively small. However, CASAC agrees that additional characterization and research is needed to fully understand the method in order to designate it as an FRM, or to use it for supporting objectives such as model evaluation and filter pack comparisons. There are also some practical issues with wide-scale deployment in an ambient network setting. Overall, CASAC is optimistic these method issues could be resolved, but remained cautious on the practical aspects of wide-scale deployment including network design and resource requirements. Using only the existing NCore rural sites will not provide enough spatial coverage to support the secondary standard. Allowing for an alternative approach using the CASTNET filter pack total nitrate measurement as an indicator may be a more practical solution in the near term and still capture most of the deposition relevant oxidized nitrate species.

CASAC believes that that more research is needed to characterize the existing NO_y method with respect to a variety of issues. These include but are not limited to:

- converter efficiency for the various oxidized nitrogen species
- instrument behavior over extended deployment periods in remote areas
- effect of converter height
- spatial representative relative to nearby terrain and vegetation
- particulate and nitric acid losses in the inlet
- low temperature operation and potential condensation in sampling lines
- reduced nitrogen species interference
- varying NOz levels relative to NO_x levels
- detection limits relative to levels in remote areas

From a practical perspective, the NO_y method is not as straightforward to deploy as other continuous ambient gas analyzers. The unique calibration procedure and long sampling lines require extra resources in the areas of calibration, auditing operation, and data quality control. It may be even more difficult to achieve consistent results in remote locations with limited technician access. Given the difficulty in NO_y instrument operation in network settings, a full suite of fully validated Quality Assurance/Quality Control (QA/QC) requirements should be a part of any FRM or FEM designation, including calibration, operation, data validation, and auditing procedures. While many of these procedures are currently being worked out for the current NCore deployment, they may not all be applicable to the lower rural NO_y levels and may not address all of the method issues listed above. CASAC encourages EPA to take full

advantage of the current expertise with NO_y measurements that exists throughout the country at monitoring agencies as well as the research community.

CASAC supports the need for and the general outline of the proposed research plan on the NO_y method for potential FRM designation. The plan should address most of the method issues listed above. Panel members had several specific recommendations for specific components of the research plan. For instance, there is a strong consensus that ambient testing should be done in multiple sections of the country in different atmospheric environments and different seasons. There is also broad support for the laboratory characterization and the particle generation experiments, but cautioning that quantitative ammonium nitrate particle generation can be challenging. CASAC also suggests that emerging true NO_2 analyzer methods should also be considered as an alternative to the existing NO_y method that uses traditional NO_x analyzers. Detailed recommendations for the NO_y research plan by individual panelists can be found in the attached individual panelist comments.

Great care must be taken in designating an FRM such that future advances in measurement technology are not precluded from consideration or use. One alternate approach is to designate an FRM of "true total oxidized nitrate" as the sum of multiple, high-quality, possible time-integrated, individual measurements of oxidized nitrate species (NO, NO_x, nitric acid, PAN, HONO, p-nitrate, etc.). Then the existing NO_y instruments, and any other existing or future technologies, would be considered for FEM status based on comparisons to the FRM in multiple locations and different seasons. The infrastructure for such testing may be provided by the proposed 2-5 NO_y "supersites" that would include the required suite of detailed NO_y species measurements. Furthermore, the " F" factors in the AAI can be derived for each specific FEM (including potentially the CASTNET total nitrate measurement), with the value of "F" based on the FEM comparisons to the FRM and/or the responsiveness of the CMAQ-simulated deposition to that FEM specific measurement.

<u>Charge Question 5:</u> *What are the panel's views on using the emerging AMoN ammonia monitoring network that uses passive sampling technology as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?*

CASAC is supportive of the utilizing the AMoN passive sampling ammonia monitoring network for air quality model (AQM) evaluation and in support of improved spatial characterization of ambient ammonia concentrations. In evaluating AQM behavior, measurements of total reduced nitrogen are likely to be just as effective as separate measurements of ammonium and gaseous ammonia, if the total reduced nitrogen measurements can be coupled with major anion measurements. Therefore, as described in the response to charge question 6 on ammonium measurements, integrated ammonia and ammonium measurements using impregnated filters may be an ideal approach.

Nevertheless, gas phase measurements of ammonia are sparse and the information emerging from the AMoN network has the potential to be valuable. Additional performance evaluations of the passive samplers used in the AMoN will be needed to make maximum use of these emerging data.

Charge Question 6: *What are the panel's views on co-locating ammonia measurements at each location where the indictors are measured?*

CASAC agrees that ammonia measurements would be useful since the current approach to setting the F2 value in the AAI is based solely on models. Having integrated measurements at as many sites as possible would provide the opportunity to supplement the modeling with the measurement data and provide a greater degree of reliability in the F2 values.

Ammonia has a high deposition velocity, and measurements are needed to assess ammonia deposition (particularly wet deposition). Integrated measurements are available using instruments available at a reasonable price. Integration of data for over a few months may provide a good test of ammonia inventory data.

Charge Question 7: *What are the Panel's views on using the CASTNET filter pack (FP) to measure ammonium ion as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?*

CASAC believes that use of the CASTNET FP that uses Teflon and Nylon FP filters probably provides a reasonable measurement of ammonium ion, but identifies several uncertainties associated with use of the CASTNET FP for this measurement. First, ammonium from nitrate can be lost from the Nylon filter in some cases (see X.Y. Yu, T, Leea, B. Ayresa, S.M. Kreidenweisa, W. Malmb, and J.L. Collett, Jr. 2006. Loss of fine particle ammonium from denuded nylon filters, *Atmospheric Environment* 40: 4797–4807). At sites where ammonium nitrate levels were high and dominant, average losses of up to 28% ammonium ion were reported; this was with 24-hour samples but at higher flows, so these examples may not reflect the potential for loss from the FP. There is a likely positive artifact in areas with strongly acidic sulfate, since in rural areas with elevated sulfate levels the sulfate is more acidic during the day (downward vertical mixing of non-boundary-layer air masses) and ammonia levels are low. At night, ammonia levels are likely to be higher (sources are at the surface), and ammonia may neutralize some of the acidic sulfate on the Teflon filter, resulting in a positive nitrate artifact. Robust measurements of ammonium ion could be made using basic and acid gas denuders upstream, a Nylon filter, and a "trap" for ammonia downstream (coated filter or denuder). This is a relatively complex method that may not be appropriate for a large network; it also breaks FP SO_2, but that and nitric acid and ammonia could be measured from the upstream denuders.

In the broader context of the AAI calculations, CASAC believes that the relative uncertainty of the FP nitrate is probably not a major issue. CASAC strongly notes that ammonium ion measurements, taken alone, are not a good test of model ammonia sources or deposition. When ammonium is in excess of sulfate on an equivalent basis (as is often the case), the concentration of ammonium is determined by the supply of sulfate and nitrate, not the supply of ammonia (See R.W. Pinder, P.J. Adams, A.N. Pandis and A.B. Gilliland, Temporally-resolved ammonia emission inventories: current estimates, evaluation tools, and measurement needs, Journal of Geophysical Research 111 (2006), p. D16310). One could add a measurement of gaseous ammonia in order to have closure on NHx, but it would be far more useful and robust to simply have a direct measurement of total NHx. From the perspective of testing models for NHx deposition, CASAC believes that there is little advantage to having speciated ammonia and ammonium measurements as compared to a measurement of total NHx. One can infer the NHx partitioning between the gas and PM phases from knowledge of sulfate and total nitrate concentrations.

Total NHx can easily be measured with a single (or double if needed) acid-coated filter (phosphoric acid for example). CASAC recommends that breakthrough be evaluated. This method could be complemented at a subset of sites with passive NH_3 measurements, but does not provide a measurement of SO_2. Its performance for SO_4 would need to be evaluated (potential SO_2 interference).

Finally, CASAC believes that time resolution is important for model evaluation. The inorganic thermodynamic regime can vary substantially on a sub-daily time-scale; ideally you want to be able to measure capture that variation. Daily (24-hour) measurements are informative; though hourly would provide considerably more information. CASAC believes that multi-day measurements are not nearly so helpful for evaluating AQMs, and would likely not be widely used for that purpose. . This is where the goal of deposition measurements and model assessment are in conflict, with the currently reasonable solution being 24-hour duration measurements. "One in six" is better than multi-day (one week) measurements. Every sixth day sampling can provide a reasonable estimate of a 3-year mean, but not for a 1-year mean given the expected log-normal distribution of most of these pollutants on a 24-hour basis.

<u>Charge Question 8:</u> *What are the panel's views on establishing a suite of NO_y species measurements at 2- 5 locations in different atmospheric and ecological regions for the purpose of evaluating air quality model and NO_y instrument behavior?*

CASAC views the addition of limited NO_y speciation measurements as critical to support proposed secondary standard in the context of validating CMAQ predictions of NO_y species, validating model predictions of the transfer function from NO_y to deposition, and understanding NO_y measurements and any potential measurement biases in network deployment. CASAC

views 3-5 NO_y speciation sites that span different ecosystems and environmental factors as appropriate.

CASAC believes that existing measurement instruments and technologies are available for necessary speciation and that consideration for potential measurements should include speciation of particulate nitrate in the context of size and counter ions. As NO_y speciation measurements are already being conducted by other federal agencies and other organizations, CASAC recommends that efforts should be pursued to leverage existing research sites that have existing NO_y speciation measurements where possible.

Charge Question 9: *What are the panel's views on utilizing the existing CASTNET and rural NCore networks as a starting infrastructure for the purpose of supporting the NOx/SOx standard?*

CASAC agrees that CASTNET and rural NCore sites should be utilized if they are in appropriate locations. Other existing sites, including NADP/NTN, IMPROVE and State and Local monitors should also be considered. CASAC agrees that the siting criteria for monitoring for the NO_x / SO_x secondary standard must be defined before the existing monitor locations are evaluated as an alternative to establishing new monitors. Several Panel members suggested that the siting criteria for this new network should address variable deposition within an eco-region due to varying precipitation and source locations.

CASAC has concerns that expanding the CASTNET program to support this new monitoring objective does not have the support of many of the State and Local monitoring agencies that will have to implement this program. The current and future objectives of EPA's Clean Air Markets Division (CAMD) and its contractor are not necessarily focusing on potential changes to the measurement techniques and long term NAAQS comparisons. CASAC suggests that EPA make elements of the CASTNET suite of measurements available through a program operated in the way IMPROVE or NADP operates. In this scenario, the state or local monitoring agency in charge of monitoring in an eco-region would opt into the program by paying for the equipment and analyses and by performing the measurement procedures as specified in the accepted program SOPs. This effort would preserve the benefit of having a central laboratory but also provide the necessary implementation flexibility for the state or local agencies that will have to carry out the measurements.

Charge Question 10: *What are the panel's views on using CASTNET filter pack (FP) to measure total nitrate (particulate nitrate plus nitric acid) as the measurement approach for the purpose of providing annual average values to support the NOx/SOx standard in diagnosing NO_y*

instrument behavior and assist in delineating the relative fractions of contributing oxidized nitrogen species to total ambient oxidized nitrogen.

In general, CASAC believes that the CASTNET filter pack provides a good measurement method for total nitrate. Some Panel members expressed concerns that this measurement is not getting the speciation exactly correct between particulate nitrate and nitric acid, but that the total nitrate measurement is generally of high quality. Some Panel members also expressed concern that the particle cut size was not well defined and may underestimate nitrate in coarse particles. Several Panel members also thought that the new NO_x - SO_x secondary standard might provide some impetus to improve the CASTNET filter pack to get more accurate speciation of total nitrate, and CASAC believes that this impetus would be helpful. A good example of a possible improvement to the methodology would be to sandwich the Teflon and nylon filters directly together. This would eliminate the space between the filters and limit the loss of volatile species.

Finally, the Panel suggested that total nitrate from CASTNET could be combined with modeled output for some unmeasured species to estimate NO_y. This analysis could be an alternative or a complementary approach to developing a new method to measure NO_y given the current uncertainty about the accuracy, precision, and interferences of the NO_y method and the costs of deploying these instruments at numerous sites around the United States. CASAC believes that the suitability of a total nitrate indicator, combined with an associated CMAQ deposition transference ratio, should be further evaluated.

Charge Question 11: *What are the panel's view of the broader consideration of using CASTNET, complemented by rural NCore, to serve as a framework for the nation's rural monitoring of important gases and aerosols in support of secondary standards and evaluating the behavior of regional air quality models?*

This is really a two-part question. Part 1 addresses suitability of CASTNET and NCORE sites and data for attainment decisions. Part 2 addresses suitability of CASTNET and NCORE data for model evaluation.

Regarding part 1, CASAC believes that it would make sense from a resource standpoint to consider CASTNET and NCORE sites for the secondary SO_x/NO_x monitoring network. However, there is also concern that relatively few CASTNET, and even fewer NCORE sites, would satisfy siting criteria for the SO_x/NO_x network. In general, sensitive ecoregions are in areas with significant elevation, vegetation and deposition gradients. It is unclear at this time how many sites are needed and in what locations to meet data requirements for the standard. Consideration should also be given to other networks, such as IMPROVE, again provided siting criteria are met.

The Panel voiced concern about coordination between CASTNET and state and local agencies. CASTNET is an EPA CAMD project operated by a private contractor. Changes in the management structure and/or operation may be needed before state and local agencies can be comfortable with CASTNET data and attainment decisions.

Regarding part 2, there is no doubt that CASTNET and NCORE data will be extremely valuable for model evaluation purposes. NCORE sites will provide continuous (i.e., hourly) measurements of O_3, NO_2 NOy, SO_2 and CO in approximately 80 urban, suburban and rural sites across the U.S. (including Hawaii, Alaska and Puerto Rico). Hourly time resolution is needed to challenge the ability of air quality models to simulate diel patterns, which are known to be strongly affected by boundary layer structure, vegetation and other surface features. Addition of "true" NO_2 to the suite of NCORE measurements would permit evaluation of model predictions for NO_x and NO_z, the latter of which is more relevant for deposition estimates. CASTNET filter pack data, in contrast, lack temporal resolution, but provide much needed data for model evaluation in rural and remote parts of the country, on monthly and seasonal time scales. Again, data from all available monitoring networks should be used for model evaluation purposes.

Additional Comments

1) Comments on Organic Acids and Bases: The Panel noted that the discussion has revolved almost entirely about inorganic contributors to acidity with the exception of peroxyacetyl nitrate (PAN). There are organic acids and bases that also contribute to the acid neutralizing capacity (ANC) and thus, as this secondary NAAQS process moves forward, there should be some exploratory measurements of these organic moieties to ascertain their potential role in ecological effects and to serve as the input to future rounds of standard reviews.

2) Need for Modeling Research Plan: The Agency has developed an ambitious Measurement Research Plan to evaluate the performance of, suggest needed improvements to, and subsequently propose FRMs and FEMs for, the various atmospheric indicators. However, there is no equivalent Modeling Research Plan to evaluate, improve, and transparently expose the CMAQ estimates of the modeled atmospheric and deposition species, the associated deposition transference ratios, and the joint performance of measurement plus model combinations upon which the NAAQS compliance will be determined.

   CASAC suggests that the design and implementation of such overarching evaluation can and should be accomplished by close collaboration between the monitoring and modeling branches of the Agency as well as other interested stakeholders. The outcome of this

effort should improve the accuracy of, strengthen the confidence in and promote future refinements to the three deposition terms in the AAI.

Enclosure C
Compilation of Comments from Individual Members of the CASAC Air Monitoring and Methods Subcommittee (AMMS) Review Panel

Comments from Mr. George A. Allen 19
Comments from Dr. Doug Burns 25
Comments from Dr. Judith Chow 27
Comments from Dr. Kenneth Demerjian 43
Comments from Dr. Eric Edgerton 47
Comments from Mr. Henry (Dirk) Felton 51
Comments from Dr. Philip Hopke 58
Comments from Dr. Rudolf Husar 60
Comments from Dr. Daniel Jacob 63
Comments from Dr. Peter H. McMurry 67
Comments from Dr. Allen Robinson 70
Comments from Dr. Jay Turner 74
Comments from Dr. Yousheng Zeng 78
Comments from Dr. Andrzej Bytnerowicz 84
Comments from Mr. Rich Poirot 87

Comments from Mr. George A. Allen

Charge Question 1: What are the Panel's views on using the CASTNET filter pack (FP) to measure particulate sulfate for the purpose of providing annual average values as an indicator for the NOx/SOx standard? Given EPA plans primarily to document the capability of the CASTNET FP and develop the FRM for particulate sulfate based on the existing information and procedures, what are the Panel's views of this approach for setting the FRM?

The FP is adequate for measuring weekly mean sulfate. One issue EPA will have to consider for a FRM is the size cut -- 2.5 um or open face. Castnet is open face; all other network SO_4 is 2.5 um. From a total S deposition perspective [which includes wet deposition], the coarse sulfate is a very minor component, even though it has higher deposition rates than the fine sulfate mode. Another consideration is that if the Castnet-style Teflon filter sampler is designated as an FRM, that should be only for the SO_x - NO_x NAAQS, not for other sampling such as the higher flow 24-h samples usually collected by other networks (IMPROVE, CSN). Note that the Castnet sampler uses only the first [Teflon] filter of the FP; the rest of FP filters are not relevant for SO_4.

Charge Question 2: What are the Panel's views on using the CASTNET filter pack (FP) to measure sulfur dioxide gas for the purpose of providing annual average values as an indicator for the NOx/SOx standard? If EPA would document the capability of the CASTNET FP and develops an FRM for sulfur dioxide gas based on the existing information and procedures, what is the Panel's view of this approach for setting the FRM?

The FP should measure SO_2 well enough for the intended purpose (dry deposition). I do not recommend that EPA consider making it an FRM; there already is an SO_2 FRM as promulgated in the June 2010 SO_2 primary NAAQS rule. The FP could be designated as an FEM, but only for the secondary standard. Additional characterization of this method compared to the existing FRM would be needed. Tests of collection efficiency at 5 pm and different RH (low, high) need to be done.

Charge Question 3: What are the Panel's views on using the current primary FRM (high time resolution UVF) to measure sulfur dioxide gas for the purpose of providing annual average values as an indicator for the NOx/SOx standard?

From a data quality standard, other than effective limits of detection, there are no issues unless there are high NO levels (unlikely at rural sites), due to the NO rejection ratio requirements for the SO_2 FRM (200:1). The question is one of resources; assuming the FP SO_2 is of reasonable quality (this needs to be demonstrated), the primary FRM could be deployed only at a small subset of "intensive" sites. There are no real issues with the FP SO_2 data being used for determining compliance with the primary SO_2 NAAQS, since that is driven by hourly values, not

annual means. There is concern that existing trace SO_2 instruments may not measure the very low SO_2 levels present at some sites with sufficient precision. With care, these instruments can generate useful hourly means down to ~ 0.3 or 0.4 ppb. The dominant source of error at these low levels is zero error and stability; if these errors are random over a year, the mean SO_2 data may be useful down to ~0.1 ppb. See my trace SO_2 RAIN guidance document for further discussion of this topic.

Charge Question 4: What are the panel's views on using existing NOy methods that are deployed, for example, in NCore as the measurement approach for NOy for the purpose of providing annual average values as an indicator for the NOx/SOx standard?

What are the panel's views on EPA's assessment that additional study is needed before establishing an FRM based on the existing NOy methods? That is, are the methods already adequately demonstrated as a reference method to determine compliance with a NAAQS?

What are the panel's views on the research plan for establishing existing NOy methods as an FRM? [Note suggested improvement to the plan would be appreciated, particularly ones that would help complete the study on time.]

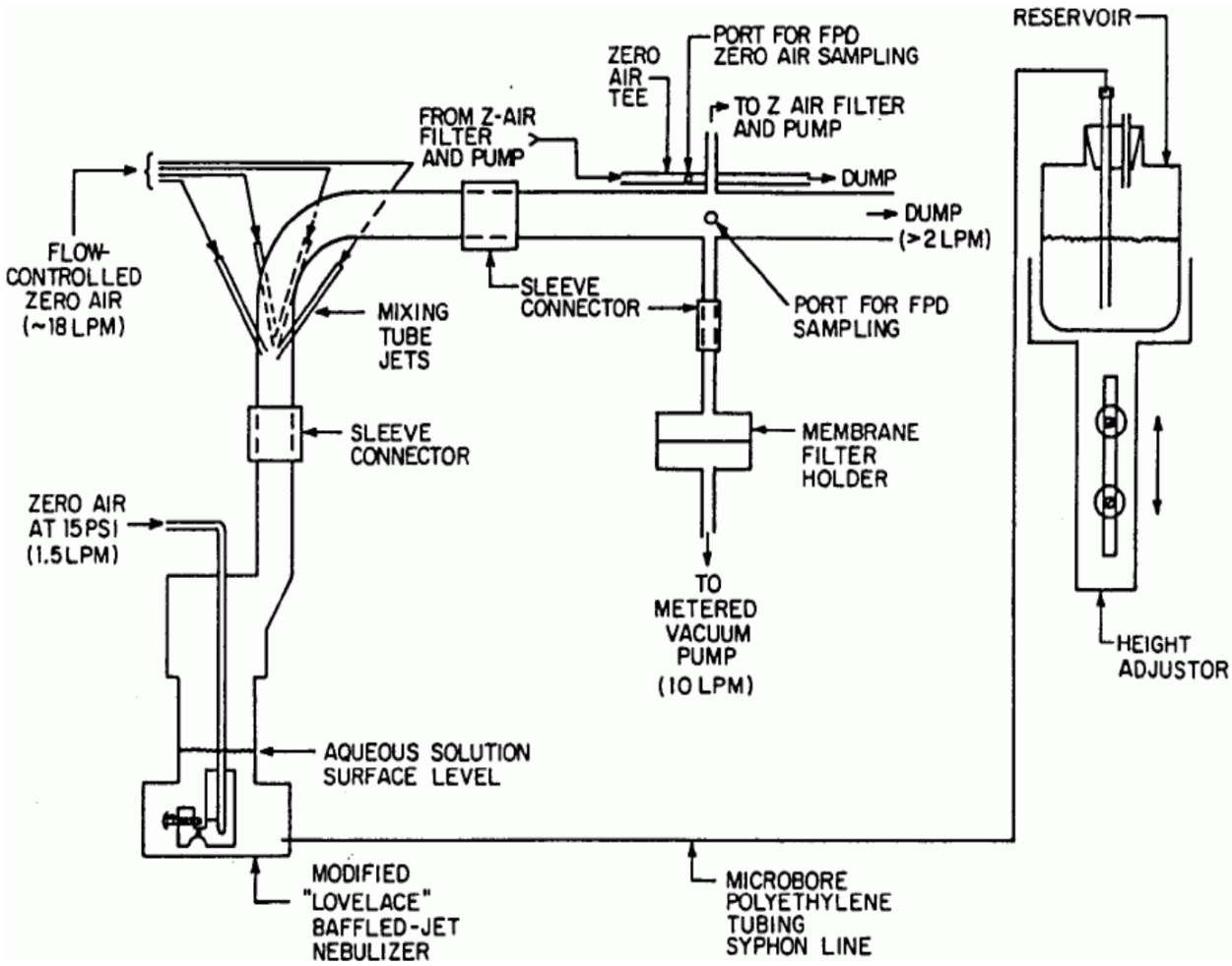
As detailed in the EPA "Research Plan" of 1/20/11, data quality from existing commercial NO_y instruments is difficult to characterize -- at least the NOz component (NO_y - NO_x). The Castnet FP provides sufficient information on deposition relevant oxidized N species when the other (large) uncertainties of the proposed secondary NAAQS are considered. Thus, from a practical point of view, I would suggest robust NO, true NO_2, and NO_y measurements only at a subset of sites, and NOT at every SO_x - NO_x site!

I agree with EPA that additional characterization of existing commercial NO_y instrument is essential before establishing an FRM for NO_y. Ideally, a single instrument that measures NO, true (photolytic) NO_2, and NO_y (and thus NOz) would be used; such an instrument could easily be commercialized using existing technologies. Some vendors may already have these instruments under development.

Testing must be carried out in warm humid areas and very cold areas. Condensation in portions of the sample line can occur in either condition, causing loss of sample NO or calibration NO and NO_2. For very cold areas, the dilution (zero) air must be dried to a dew point lower than the ambient dew point, since some of the sample line is outdoors at ambient temperature. Silica gel (0 deg. C) is not sufficient; Drierite or similar products must be used (-73 deg. C).

The NO_y component of the EPA research plan is reasonably comprehensive. Table 1 shows the API 200eu with speciated NO_y, but this instrument does not measure NO_y. Additional details on using the VOAG for generating ammonium nitrate aerosol are necessary; this is a very complex task to do correctly (Jim Schwab at ASRC-SUNY Albany has valuable experience for this). Since relative humidity (RH) may change the extent of nitrate loss (nitrate is more stable at

higher RH), the effect of RH on these tests should be evaluated. Keeping sample lines cool further stabilizes nitrate. Consideration of other generation methods such as the Lovelace Nebulizer (http://www.intoxproducts.com/lovelacenebulizer) may be appropriate; in a modified form (submerging the nebulizer and other simple changes) this has shown to be a very robust way to generate aerosols from solution, and can be packaged into a portable system. A flow diagram of
the HSPH aerosol generation system from the 1980's follows:



As with ammonium nitrate, generating HNO_3 and NH_3 and delivering it to a sampler without significant losses is challenging. More detail on this would be useful; very short residence times, very clean borosilicate glass, and heating are essential components of any such system.

Whatever aerosol generation system is used, it may be useful to assess its relative output in real time with a nephelometer (light scattering); if the moisture content (RH) of the aerosol changes, the nephelometer data would need to account for enhanced scattering of nitrate or sulfate aerosols at RH values greater than ~ 40%.

Finally, an important component of good NO_y measurements is siting. Elevation above ground and "fetch" (distance to nearest forested area) are critical. 10 meters above ground and at least 3-4 times horizontal distance relative to the height of the nearest forest canopy are appropriate criteria.

Charge Question 5: What are the panel's views on using the emerging AMoN ammonia monitoring network that uses passive sampling technology as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?

The Radiello® passive samplers used in the AMoN network appear to be suitable for 2 week duration samples, but may need an offset correction. See the accuracy and blanks plots on pages 7 and 8 of a CAMD presentation from October 27, 2010:
http://www.nescaum.org/documents/mac/mac-committee-meeting-3/rury-amon.pdf/

These results are presumably from carefully controlled tests, and thus may not reflect the data quality from routine field measurements. It would be helpful to get a more complete evaluation update from CAMD.

Charge Question 6: What are the panel's views on co-locating ammonia measurements at each location where the indicators are measured?

If only the FP is run, it would be useful to have a subset of sites include passive ammonia measurements. If an NHx method is run (see Q #7), this is less important but still useful.

Charge Question 7: What are the Panel's views on using the CASTNET filter pack (FP) to measure ammonium ion as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?

The sum of Teflon and Nylon FP filters probably provides a reasonable measurement of ammonium ion, but there are some uncertainties and biases. First, ammonium from nitrate can

be lost from the Nylon filter in some cases; see: Yu et al., "Loss of fine particle ammonium from denuded nylon filters", Atmospheric Environment 40 (2006) 4797–4807. At sites where ammonium nitrate levels were high and dominant, average losses of up to 28% ammonium ion were reported; this was with 24-hour samples but at higher flows, so these examples may not reflect the potential for loss from the FP. There is a likely positive artifact in areas with strongly acidic sulfate; in rural areas with elevated sulfate levels, the sulfate is more acidic during the day (downward vertical mixing of non-boundary-layer air masses) and ammonia levels are low. At night, ammonia levels are likely to be higher (sources are at the surface), and ammonia may neutralize some of the acidic sulfate on the Teflon filter, resulting in a positive artifact. Robust measurements of ammonium ion could be made using basic and acid gas denuders upstream, a Nylon filter, and a "trap" for ammonia downstream (coated filter or denuder). This breaks FP SO_2, but that and nitric acid and ammonia can be measured from the upstream denuders.

In the broader context of the AAI calculations, the relative uncertainty of the FP nitrate is probably not a major issue. Alternatively or in addition to the FP, total NHx (which is what the models need) could be measured with a single (or double) acid-coated filter (phosphoric acid for example). Breakthrough would need to be evaluated. This method could be complemented at a subset of sites with passive NH_3 measurements, but does not provide a measurement of SO_2. Its performance for SO_4 would need to be evaluated (SO_2 interference?).

Charge Question 8: What are the panel's views on establishing a suite of NOy species measurements at 2-5 locations in different atmospheric and ecological regions for the purpose of evaluating air quality model and NOy instrument behavior?

This is a good approach that would be very useful in evaluating models and NO_y measurements. This level of effort is in the "research" category, and appropriate resources and skill levels would be needed.

Charge Question 9: What are the panel's views on utilizing the existing CASTNET and rural NCore networks as a starting infrastructure for the purpose of supporting the NOx/SOx standard?

This is an obvious choice in a resource constrained scenario, even if the resulting network is not ideally located from the SO_x - NO_x perspective. If we go forward with the FP method, network operations would need to be similar to the NADP or IMPROVE model, not the existing Castnet model. There is concern from state and local air agencies about having someone else (a contractor to CAMD in this case, not under air agency control) making measurements that could be used to demonstrate non-compliance with a NAAQS.

Charge Question 10: What are the panel's views on using CASTNET filter pack (FP) to measure total nitrate (particulate nitrate plus nitric acid) as the measurement approach for the purpose of providing annual average values to support the NOx/SOx standard in diagnosing NOy instrument behavior and assist in delineating the relative fractions of contributing oxidized nitrogen species to total ambient oxidized nitrogen.

The FP does not provide a measure of ammonium nitrate, but it does provide a reasonable measure of the sum of nitric acid, nitrous acid, and ammonium nitrate if the Teflon and Nylon nitrate filter data are summed. There can be modest losses of ammonium nitrate from a Nylon filter sampler (Babich et al., J. Air & Waste Manage. Assoc. 50:1095-1105, table 5, Bakersfield 1999). "Sandwiching" the Teflon and Nylon filters in a single filter holder minimizes interstage losses of nitric acid. See the description of "Nylon HEADS" in Babich et al. (above).

FP "total nitrate" is a reasonable metric for a NO_x / SO_x standard. I do not see it being useful in diagnosing NO_y instrument behavior for several reasons - the most obvious being the 1-week duration of the FP sample. It is also not very useful for delineating the relative fractions of contributing oxidized nitrogen species to total ambient oxidized nitrogen, since it is the sum of nitric acid and ammonium nitrate. Perhaps the most important issue here is the lack of any FP NO_2 measurement; NO_2 in rural areas can be as much as half or more of the NO_y.

Charge Question 11: What are the panel's view of the broader consideration of using CASTNET, complemented by rural NCore, to serve as a framework for the nation's rural monitoring of important gases and aerosols in support of secondary standards and evaluating the behavior of regional air quality models?

See response to Charge Question 9 above.

Comments from Dr. Doug Burns

General Comments

Many of the charge questions focus on leveraging CASTNET (and to an extent rural NCORE) measurements to address this new secondary standard. I support leveraging these existing networks where possible if the measurements and methods are rigorous and would lend themselves to FRM/FEM designation. The total NO_y measurement seems like it needs lots of testing and may not be ready to deploy in a monitoring network for a couple of years at best. I also feel that passive collectors can be valuable. Though these devices may be less accurate and precise than other measurements, they are relatively inexpensive and can provide an opportunity to greatly expand the spatial intensity of measurements. This is important for aspects of model checking. It would seem that NH_3 and NO_2 should be priorities for passive collection.

Though this subcommittee was tasked with questions that focused solely on atmospheric chemical measurements, I note that surface water chemistry measurements in sensitive ecosystems are essential to promulgation of this new NO_x - SO_x standard. Some sensitive regions of the US have good and recent surface water chemistry measurements, but some regions have few or none. I would think that an attempt needs to be made to evaluate existing water quality data that could be used to promulgate this standard. This would help to identify gaps and limitations in implementing this potential new rule.

Charge Question 10 – Use of CASTNET filter pack to measure total nitrate

Measurement of total nitrate is currently done at all CASTNET sites using the filter pack. These measurements are generally viewed as providing accurate data on total nitrate concentrations in ambient air (see CASTNET QA reports on line), though the speciation between particulate nitrate and nitric acid may not be accurate. Precision is in the range of +/- 3-5%. Currently, data on total dry nitrate combined with particulate ammonium from CASTNET is “the” measurement to calculate dry N deposition for those working in remote/rural ecosystems sensitive to acidification. Clearly, these species from CASTNET do not represent all dry deposited N species and therefore, the CASTNET measurements provide an underestimate of deposition. The key question to answer then becomes: Does total nitrate from CASTNET vary in a predictable manner relative to the other key dry N species such as NH_3, NO_2, and PAN? If the answer is yes or close enough to yes, then CASTNET total nitrate from the filter pack would be a good surrogate for the secondary NO_y standard. Data shared with this subcommittee from two sites in Canada (measured by CAPMON), as well as work by Jed Sparks and others suggest that key N species such as NH_3, NO_2, and PAN vary significantly both spatially and temporally and not necessarily synchronously with total nitrate. This would indicate that total nitrate is not a good surrogate for NO_y. However, this could be explored in greater detail using existing data and/or model results (such as CMAQ) for NO_2, NO, and PAN.

Charge Question 5 – Use of the AMoN ammonia monitoring network

This is a question that gets to the issue of being able to make lots of measurements inexpensively (passive samplers) vs. being able to make fewer measurements (denuder), but more expensively. I have observed the development of the AMoN network first hand. It is clear based on comparisons done among three passive NH_3 devices that the Radiello were the most accurate of the passive samplers available at that time. The tests performed with the Radiello samplers indicate good precision (< 10%) and a low bias compared to side-by-side denuder measurements. The low bias appears to be on the order of 0.3 to 0.6 ug/m3 based on the comparisons I have seen. This obviously becomes more of a problem at sites with low NH_3 concentrations where the deviations are greatest in absolute and relative terms. My recommendation would be to deploy as many denuder samplers as budgets allow, including some sites that have both a denuder and a passive sampler. The passive samplers could then be used to create a denser network of sites in areas of particular interest such as the Adirondacks and Shenandoah Park.

Comments from Dr. Judith Chow

Charge Question 1: What are the Panel's views on using the CASTNET filter pack (FP) to measure particulate sulfate for the purpose of providing annual average values as an indicator for the NOx/SOx standard? Given EPA plans primarily to document the capability of the CASTNET FP and develop the FRM for particulate sulfate based on the existing information and procedures, what are the Panel's views of this approach for setting the FRM?

The weeklong CASTNET samples provide a good measurement of annual average water-soluble $SO_4^=$ with a precision of 2–4% (Baumgardner et al., 1999; Bytnerowicz et al., 2002; Sickles, II and Shadwick, 2002). Total $SO_4^=$ values are comparable within the network and with other networks (Lavery et al., 2009; Sickles, II et al., 1999; Sickles, II and Shadwick, 2002).

Charge Question 2: What are the Panel's views on using the CASTNET filter pack (FP) to measure sulfur dioxide gas for the purpose of providing annual average values as an indicator for the NO_x/SO_x standard? If EPA would document the capability of the CASTNET FP and 4 develops an FRM for sulfur dioxide gas based on the existing information and procedures, what is the Panel's view of this approach for setting the FRM?

The weeklong CASTNET samples by filter pack provide a reasonable measurement of annual average SO_2 and appear to be comparable within and between networks (Bennett et al., 1994; Bytnerowicz et al., 2002; Chow et al., 1993; Lavery et al., 2009). Sickles et al. (1999) provide methodological caveats that warrant a revisit of the current CASTNET procedures. The partial collection of SO_2 on Nylon filters (Japar and Brachaczek, 1984; Sickles, II and Hodson, 1999a; Sickles, II and Hodson, 1999b) is added to the SO_2 measurement on the two K_2CO_3-impregnated cellulose-fiber filters at the final stage of the filter pack.

Accuracy of the filter pack measurements has been evaluated with an annular denuder system for SO_2 and $SO_4^=$. The filter pack system has been shown to provide 10–20% lower SO_2 values than those of the annular denuder system (Baumgardner et al., 1999). For weeklong samples, Kim and Allen (1997) reported adsorption of SO_2 on Nylon filters was 29.4 ± 8.5% at 2 L/min flow rate (decreasing to 16.3 ± 4.5% as flow rate is increased to 5 L/min). The lower in SO_2 retention on Nylon filters at higher flow rates was attributed to reduced residence time of SO_2 at the Nylon filter surface. Since CASTNET samples at a flow rate of 1.5 L/min for the eastern sites and 3.0 L/min at the western sites, the effects of flow rate on SO_2 retention needs to be further investigated.

Sickles et al. (1990) tested coated sorbents and impregnated filters for SO_2 and NO_2 in the laboratory and found SO_2 recovery efficiency on triethanolamine (TEA)-impregnated filters

decreased from ~90% under dry conditions to ~80% at 50% relative humidity (RH). The effect of SO_2 recovery efficiency on K_2CO_3-impregnated cellulose-fiber filter under different RH needs to be tested.

The extraction efficiency of SO_2 on Nylon filters needs to be further tested. For the California Acid Deposition Network (Watson et al., 1991), a 0.1% H_2O_2 solution was used for extraction of K_2CO_3-impregnated cellulose-fiber filters, instead of distilled deionized water (DDW), to ensure oxidation of SO_2 and $SO_3^{=}$ to $SO_4^{=}$ and to prevent interference of $SO_3^{=}$ on NO_3^{-} peaks in ion chromatographic (IC) analysis.

A negative bias may exist, owing to the reaction of SO_2 with alkaline soils sampled on the Teflon-membrane filter (Eatough et al., 1995; Eldred and Cahill, 1997; Usher et al., 2002). Early studies showed that filter pack SO_2 is 14–15% lower than the corresponding annular denuder system, suggesting a bias in SO_2 measurement by filter pack (Dasch et al., 1989; Sickles, II et al., 1990). Sickels and Hodson (1999b) discovered that SO_2 is unrecoverable from the Nylon filter, ranging from 5% at 28% RH to 10% at 49% RH. The unrecovered SO_2 on Nylon filters needs to be further tested and evaluated for different RH.

Charge Question 3: What are the Panel's views on using the current primary FRM (high time resolution UVF) to measure sulfur dioxide gas for the purpose of providing annual average values as an indicator for the NOx/SOx standard?

Using high-time resolution UVF to measure SO_2 for the purpose of providing annual average values as an indicator for the NO_x/SO_x standard seems costly and impractical. Many hourly SO_2 levels may be below the lower quantifiable limits (LQL), which are usually higher than the manufacturer's minimum detection limits (MDL), at regional sites. Sickles et al. (1990) reported detection limits of 0.04 ppb for seven-day samples based on the MDL of the IC method. It would be necessary to evaluate the effect on non-detects on the annual average if a continuous FRM were to be used for an annual average.

Charge Question 4: What are the panel's views on using existing NOy methods that are deployed, for example, in NCore as the measurement approach for NOy for the purpose of providing annual average values as an indicator for the NOx/SOx standard? What are the panel's views on EPA's assessment that additional study is needed before establishing an FRM based on the existing NOy methods? That is, are the methods already adequately demonstrated as a reference method to determine compliance with a NAAQS? What are the panel's views on the research plan for establishing existing NOy methods as an FRM? [Note suggested

improvement to the plan would be appreciated, particularly ones that would help complete the study on time.]

An evaluation is needed to determine how values below detection limits will be incorporated into an annual average. More study is needed for NO_y monitors in non-urban areas. Small variations in converter efficiency can bias these data.

Charge Question 5: What are the panel's views on using the emerging AMoN ammonia monitoring network that uses passive sampling technology as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?

Passive samplers can provide reasonable estimates of ambient concentrations and are widely used in other countries and in some parts of the U.S. (Adon et al., 2010; Alonso et al., 2005; Bytnerowicz et al., 2010; Cao et al., 2009; Kirchner et al., 2005; Martins et al., 2007; Meng et al., 2010; Mosquera et al., 2005; Moumen et al., 2004; Nishikawa et al., 2009; Ramadan, 2010). An argument might be made that a passive monitor better represents deposition than does an ambient concentration coupled with a deposition velocity. The Radiello passive sampler (Allou et al., 2008; Bruno et al., 2005; 2008a; 2008b; Chiriac et al., 2009; Diaz-de-Quijano et al., 2009; Pennequin-Cardinal et al., 2005; Plaisance et al., 2008; Ribas and Penuelas, 2006; Strandberg et al., 2005; Strandberg et al., 2006; Sturaro et al., 2010) using phosphoric acid as an impregnant followed by flow injection analysis (FIA) has been applied to NH_3 for the National Atmospheric Deposition Program's (NDAP) Ammonia Monitoring Network (AMoN). Using NH_3 data from the AMoN as a tool for evaluating air quality modeling is a good start. The passive diffusion sampler may require greater than one week sampling at remote areas in order to meet analytical sensitivity. More collocated data are needed for CASTNET to evaluate NH_3 measurements.

Charge Question 6: What are the panel's views on co-locating ammonia measurements at each location where the indictors are measured?

This is a good idea. Even though the current Aquatic Acidification Index (AAI) proposed by the U.S. EPA (2011a) does not require the measurement of NH_x, it is essential that the EPA starts to incorporate measurements of NH_x in CASTNET to gain better insight into the concentration of NH_3 and NH_4^+ at the 84 sensitive eco-regions.

Charge Question 7: What are the Panel's views on using the CASTNET filter pack (FP) to measure ammonium ion as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?

The current CASTNET filter pack configuration may be modified by adding an extra FEP stage behind the Nylon filter stage on the Savillex FEP filter holder (Eden Prairie, MN). A double Whatman 31 ET cellulose-fiber filter (0.5 mm thickness, Whatman, Inc., Fairfield, CT) with citric acid impregnant can collect NH_3, and the NH_4^+ ion is already measured on Teflon-membrane filters. Note that the Whatman 31 ET is thicker, with a greater capacity, than the Whatman 41 filters (0.22 mm thickness) used in CASTNET for SO_2 collection on K_2CO_3-impregnated cellulose-fiber filters. Chow et al. (1993) showed that a Teflon-membrane/citric acid-impregnated cellulose-fiber/ K_2CO_3-impregnated cellulose-fiber filter pack will adequately retain NH_3 without interference with downstream SO_2 measurements at a 20 L/min flow rate. This filter pack sampling configuration and the collection efficiencies of different impregnants has been tested at the Operational Evaluation Network (OEN; ERT, 1987; Fung, 1988a; 1988b; Fung and Heisler, 1987).

Andersen and Hovmand (1994) showed that compared to the denuder sampling system, their filter pack underestimated NH_3 at conditions with low NH_3 concentrations. They attributed this to the absorption of NH_3 in an unsaturated acid aerosol atmosphere. Since the acid-absorbing Nylon filter would precede the acid-impregnated filter for NH_3 collection and may retain NH_3 (Masia et al., 1994), NH_3 (expressed as NH_4^+) needs to be measured on the Nylon filter. The LQLs, sensitivity, precision, and accuracy of CASTNET NH_3 measurements at a low flow rate need to be tested for different concentration levels and at different ambient temperatures to ensure collection efficiency under extremes of temperature and RH.

Charge Question 8: What are the panel's views on establishing a suite of NOy species measurements at 2- 5 locations in different atmospheric and ecological regions for the purpose of evaluating air quality model and NOy instrument behavior?

Resolve the issue of its effects on annual averages first.

Charge Question 9: What are the panel's views on utilizing the existing CASTNET and rural NCore networks as a starting infrastructure for the purpose of supporting the NOx/SOx standard?

See answer to Charge Question 11.

Charge Question 10: What are the panel's views on using CASTNET filter pack (FP) to measure total nitrate (particulate nitrate plus nitric acid) as the measurement approach for the purpose of providing annual average values to support the NOx/SOx standard in diagnosing

NOy instrument behavior and assist in delineating the relative fractions of contributing oxidized nitrogen species to total ambient oxidized nitrogen.

The CASTNET filter pack provides a good measure of total nitrate as defined, but does not provide as good a distinction between particulate NO_3^- (i.e., pNO_3^-) and gaseous HNO_3. Figure 1 illustrates the CASTNET filter pack and Figure 2 summarizes the analyses applied to each filter.

Figure 1-4 Three-Stage Filter Pack

Cellulose (2)	Nylon	Teflon®
Gaseous	Gaseous	Particulate
• SO_2	• HNO_3 • SO_2	• SO_4^{2-} • NO_3^- • NH_4^+ • K^+ • Ca^{2+} • Mg^{2+} • Na^+ • Cl^-

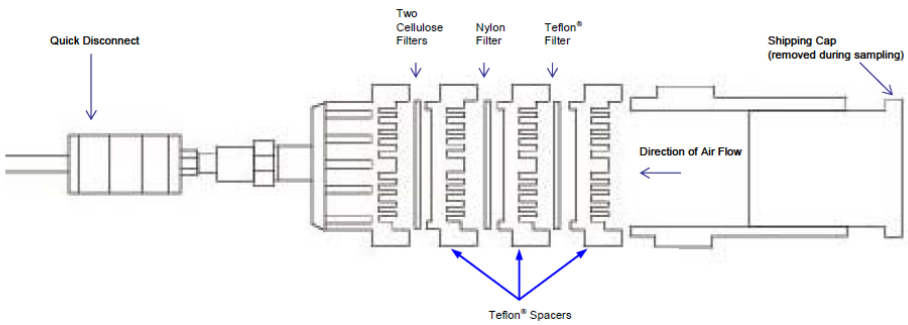


Figure 1. The CASNET filter pack (MACTEC, 2010). Filters are placed in series in an open-faced Savillex FEP Teflon filter holder (Eden Prairie, MN). The two Whatman cellulose-fiber filters (Fairfield, CT) are impregnated with a K_2CO_3 solution that reacts with SO_2 to form $SO_4^=$. The filter pack is located atop a 10 m boom with the receptacle facing downward. Samples are installed every Tuesday and taken continuously for 168 hour durations (1 week) at flow rates of 1.5 L/min for eastern sites and 3.0 L/min for western sites.

Table 3-2 Summary of Analytical Methods by Sample Type

Operation	Sampling Media	Analytes	Instrumentation	Reference Method
Dry Deposition				
Filter Pack System	Teflon® Filter	NO_3^- (as N), SO_4^{2-}, Cl^-	IC Dionex DX500/300	EPA Method 300.0*
		NH_4^+	Bran+Luebbe AutoAnalyzer 3	EPA Method 350.1
		Ca^{2+}, Mg^{2+}, Na^+, K^+	ICP-AES PE 3000 DV	EPA Method 6010
	Nylon Filter	NO_3^- (as N), SO_4^{2-}	IC Dionex DX500/300	EPA Method 300.0
	Cellulose Filter	SO_4^{2-}	IC Dionex DX500/300	EPA Method 300.0

Figure 2. Analysis methods applied to distilled deionized water (DDW) extracts from each CASTNET filter (MACTEC, 2009). Since the Nylon filter adsorbs some of the SO_2 (Sickles, II et al., 1999; 1999a; Sickles, II and Hodson, 1999b), $SO_4^=$ is also measured on Nylon and added to the SO_2 (expressed as $SO_4^=$) collected on the backup cellulose-fiber filters.

The Nylon and impregnated filter technology for HNO_3 and SO_2 is well established and has been thoroughly evaluated (Appel et al., 1980; Axelrod and Hansen, 1975; Chow et al., 1993; Ferek et al., 1991; Ferek et al., 1997; Forrest et al., 1980; Forrest and Newman, 1973; Huygen, 1963; Johnson and Atkins, 1975; Leppanen et al., 2005; Lewin and Zachau-Christiansen, 1995; Matsuda and Cahill, 1985; Orr et al., 1967; Sickles, II et al., 1999; Talbot et al., 1990; Tsai et al., 2004). Aside from the simplicity and cost-effectiveness of the filter pack system, its major advantage is that all suspendable particles are collected and there are no interfering sampling surfaces that adsorb HNO_3. Its major disadvantage is blurred distinction between pNO_3^- and HNO_3. The separation is probably reasonable during winter, when temperatures are <15 °C and NH_4NO_3 dissociation is low (Appel et al., 1979; Appel, 1994; Chow et al., 2005; Spicer and Schumacher, 1979; Zhang and McMurry, 1991; Zhang and McMurry, 1987). On the other hand, when alkaline soils, sea salt, or deicing material are sampled on the front filter, these particles can collect the HNO_3 that will be measured as pNO_3^- (Dasch and Cadle, 1990; Goodman et al., 2000; Krueger et al., 2004; Laskin et al., 2005; Liu et al., 2008; Ooki and Uematsu, 2005; Umann et al., 2005; Underwood et al., 2001). Although total NO_3^- filter pack measurements are comparable to the annular denuder system, the under- or overestimation of HNO_3^- or pNO_3^- may affect the modeled dry nitrogen deposition, since the dry deposition velocity (V_d) for HNO_3 is typically higher than that for pNO_3^-. Lavery et al. (2009) found that CASTNET underestimates NO_3^- and overestimates HNO_3 at coastal sites, where >80% of NO_3^- particles were >2.5 µm; attributed to the reaction of NaCl with some of the volatilized NO_3^- and scavenging of HNO_3 by alkaline particles collected on the Teflon-membrane filter. Heterogeneous reactions of HNO_3 on $CaCO_3$ particles was tested by Goodman et al. (2000), who found that the presence of water vapor enhanced this reaction. Sickles and Shadwick (2008) reported higher pNO_3^- (±42% to ±102%, on median relative bias) than the collocated IMPROVE measurements due to the reaction of sea salt with HNO_3. Accurate measurement of HNO_3 is challenging. Arnold et al.

(2007) reported agreement is ±30% when semi-continuous measurements of HNO_3 were compared with filter pack and annular denuder systems at urban Tampa, Florida.

As part of a mineral dust and tropospheric chemistry study, Umann et al. (2005) observed that, during a dust event, 100% of HNO_3 was depleted at a high mountaintop plateau (Izana, Canary Islands, Spain; 2367 m above sea level). There is evidence regarding the effect of coarse particles on HNO_3 in studies involving comparisons of PM_{10} and $PM_{2.5}$ pNO_3^- (Chow et al., 1993; Lavery et al., 2009).

The CASTNET filter pack also samples droplets in rain and fog, and it appears that this decreases some of the concentrations when there is evidence of filter wetting (Smith, 2002). For samples collected from 1987 to March 1998, Smith (2002) reported a total of 27,412 wet filters. This includes 0.4, 1.1, and 28.4% of wet Teflon-membrane, Nylon-membrane, and cellulose-fiber filters, respectively. Sickles and Michie (1987) showed that wet surfaces may retain more NO_2 and SO_2. Laboratory testing showed that increasing RH by fivefold (i.e., 16–79%) may increase the deposition velocities of NO_2 and SO_2 by ~50%. The effects of RH on the retention of NO_2 and SO_2 in the CASTNET filter pack system needs to be further evaluated.

Charge Question 11. What are the panel's view of the broader consideration of using CASTNET, complemented by rural NCore, to serve as a framework for the nation's rural monitoring of important gases and aerosols in support of secondary standards and evaluating the behavior of regional air quality models?

The framework should not be limited to CASTNET and NCore sites. CASTNET is adequate for determining annual averages, but week-long average measurements are not optimal for evaluating regional-scale models that intend to incorporate meteorological phenomena changing over a period of days or less. An integrated data set of regionally-representative measurements from all available networks needs to be assembled and evaluated. VIEWS (2010) for the IMPROVE network provided a good start for this, but it never had the constituency needed to support it. The NAMS/SLAMS network contains regionally-relevant sites, usually located downwind of population centers, and these should be included. IMPROVE (DeBell et al., 2006; IMPROVE, 2011; Joseph et al., 1987; Malm et al., 2000; Sisler et al., 1996; Watson, 2002), SEARCH (Hansen et al., 2003; 2006), AIRMon (Gilliland et al., 2002; NOAA, 2011), CAPMon (Environment Canada, 2011; Zhang et al., 2009), PAMS (Photochemical Assessment Monitoring Stations; U.S.EPA, 2011b), and probably other networks should be considered in such a framework.

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Comments from Dr. Kenneth Demerjian

Charge Question 1: What are the Panel's views on using the CASTNET filter pack (FP) to measure particulate sulfate for the purpose of providing annual average values as an indicator for the NOx/SOx standard? Given EPA plans primarily to document the capability of the CASTNET FP and develop the FRM for particulate sulfate based on the existing information and procedures, what are the Panel's views of this approach for setting the FRM?

This methodology should be consider as one of the several PM-SO4 techniques available (i.e. CSN, IMPROVE and continuous SO_4) to track trends in PM_ SO_4. Although the network methodologies may not report measured concentrations that agree in absolute terms, the identification of measurement bias and the demonstration of the methodologies consistency in reporting relative changes in ambient concentrations with respect to measured/estimated emission changes will be valuable in estimating uncertainty in trend analyses.

Charge Question 2: What are the Panel's views on using the CASTNET filter pack (FP) to measure sulfur dioxide gas for the purpose of providing annual average values as an indicator for the NOx/SOx standard? If EPA would document the capability of the CASTNET FP and develops an FRM for sulfur dioxide gas based on the existing information and procedures, what are the Panel's view of this approach for setting the FRM?

Unlike PM- SO_4 where particle size affects absolute concentration (see discussion item 1 above) comparisons, selected continuous SO_2 measurements should be compared with annual CASTNET SO_2 measurements as well as trends analyses to demonstration of consistency in reporting relative changes in ambient concentrations with respect to measured/estimated emission change.

Charge Question 3: What are the Panel's views on using the current primary FRM (high time resolution UVF) to measure sulfur dioxide gas for the purpose of providing annual average values as an indicator for the NOx/SOx standard?

The current primary FRM (high time resolution UVF) to measure SO_2 gas for the purpose of providing annual average values as an indicator for the NO_x / SO_x standard is acceptable. The agency should recognize that SO_2 ambient concentrations have been reduced substantial over the past decade and that trace level versions of SO_2 monitors are need to minimize non-detects and capture relevant statistical annual averages. This is a particular important issue at rural/regional monitoring sites where for example in New York State (Pinnacle State Park and Whiteface Mountain) annual average SO_2 concentrations in 1997 and 2007 were (3.48 – 1.77 ppb; at PSP) and (1.03 – 0.35 ppb; at WFM).

Charge Question 4: What are the panel's views on using existing NOy methods that are deployed, for example, in NCore as the measurement approach for NOy for the purpose of providing annual average values as an indicator for the NOx/SOx standard? What are the panel's views on EPA's assessment that additional study is needed before establishing an FRM based on the existing NOy methods? That is, are the methods already adequately demonstrated as a reference method to determine compliance with a NAAQS? What are the panel's views on the research plan for establishing existing NOy methods as an FRM? [Note suggested improvement to the plan would be appreciated, particularly ones that would help complete the study on time.]

Existing NO_y measurement technology is adequate, but requires establishing more rigorous QA/QC procedures. This includes providing training for network technicians and the development of calibration standards and protocols for estimating convertor efficiency.

Charge Question 5: What are the panel's views on using the emerging AMoN ammonia monitoring network that uses passive sampling technology as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?

There is very little documentation in the peer reviewed literature regarding the performance of the Radiello® passive samplers. Although NADP has adopted this technique, it should undergo performance evaluation with intercomparison studies with other NH_3 monitoring techniques, the results of which should be reported in the peer reviewed literature. These comparisons should also the challenge the passive sampler's sensitivity to wind speed and temperature extremes? In addition, although two-week average data can be used to aggregate seasonal and annual average ammonia concentrations, these data are far from what is necessary to challenge air quality model behavior. It is unlikely that the deployment of sufficient number of samplers will be practical (cost or technically) to fully characterize the spatial distribution of ambient NH_3 considering the complexity of its sources and sinks. Only high temporal resolution (minutes to hour) ambient NH_3 measurements afford the opportunity to: 1) measure NH_3 fluxes (to characterize local sources and sinks); 2) identify NH_3 source plumes through wind sector analyses; and 3) characterize NH_3 concentrations in the stable (typically nocturnal) boundary layer for the evaluation of AQ models and to assess the potential bias the SBL introduces to model - integrated sampling comparisons.

Charge Question 6: What are the panel's views on co-locating ammonia measurements at each location where the indictors are measured?

This would be reasonable requirement and would provide an opportunity to evaluate the model based F2 estimate and the utility of the calculated indicator approach.

Charge Question 7: What are the Panel's views on using the CASTNET filter pack (FP) to measure ammonium ion as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?

Models should use whatever data is available to test and evaluate their performance. That being said, I am not sure that CASTNET FP ammonium ion measurements would be effective in characterizing ambient air patterns of ammonia. If it has not already been done, an analysis of the SEARCH data set should provide some insight as to challenges this comparison poses given the distinctly different residence times of these two species.

Charge Question 8: What are the panel's views on establishing a suite of NOy species measurements at 2- 5 locations in different atmospheric and ecological regions for the purpose of evaluating air quality model and NOy instrument behavior?

I would be strongly supportive of such studies. Prioritization of NO_y components to be considered is HNO_3, NO_2, PM_NO_3 and PAN.

Charge Question 9: What are the panel's views on utilizing the existing CASTNET and rural NCore networks as a starting infrastructure for the purpose of supporting the NOx/SOx standard?

This is a very reasonable starting point.

Charge Question 10: What are the panel's views on using CASTNET filter pack (FP) to measure total nitrate (particulate nitrate plus nitric acid) as the measurement approach for the purpose of providing annual average values to support the NOx/SOx standard in diagnosing NOy instrument behavior and assist in delineating the relative fractions of contributing oxidized nitrogen species to total ambient oxidized nitrogen.

This is an acceptable approach.

Charge Question 11: What are the panel's view of the broader consideration of using CASTNET, complemented by rural NCore, to serve as a framework for the nation's rural

monitoring of important gases and aerosols in support of secondary standards and evaluating the behavior of regional air quality models?

Again, this is a very reasonable concept and starting point. It remains to be seen if this approach would provide sufficient spatial coverage to support the secondary SO_x / NO_x standard.

Comments from Dr. Eric Edgerton

Charge Question 1: What are the Panel's views on using the CASTNET filter pack (FP) to measure particulate sulfate for the purpose of providing annual average values as an indicator for the NOx/SOx standard? Given EPA plans primarily to document the capability of the CASTNET FP and develop the FRM for particulate sulfate based on the existing information and procedures, what are the Panel's views of this approach for setting the FRM?

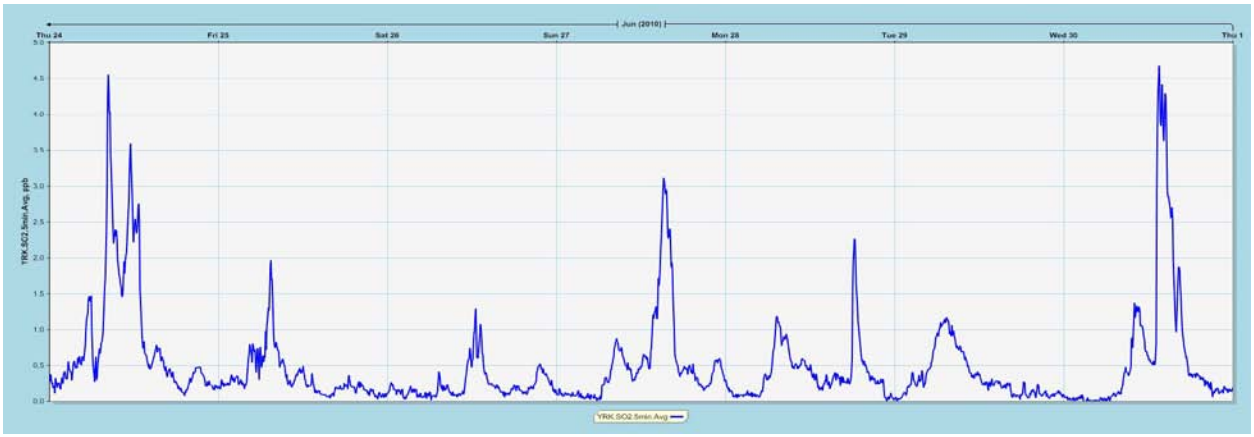
Other than the size-cut issue, the CASTNet FP should be suitable as an indicator for the standard. That said, I would be more comfortable if SO_4 were measured with a defined size cut (PM2.5 or PM10) and with SO_2 removal up front (lessons learned from the CSN).

Charge Question 2: What are the Panel's views on using the CASTNET filter pack (FP) to measure sulfur dioxide gas for the purpose of providing annual average values as an indicator for the NOx/SOx standard? If EPA would document the capability of the CASTNET FP and develops an FRM for sulfur dioxide gas based on the existing information and procedures, what are the Panel's view of this approach for setting the FRM?

I support the use of the CASTNet FP for measuring annual average SO_2 concentrations. Characterization by EPA will likely show this approach has the sensitivity and specificity to support the NO_x / SO_x standard.

Charge Question 3: What are the Panel's views on using the current primary FRM (high time resolution UVF) to measure sulfur dioxide gas for the purpose of providing annual average values as an indicator for the NOx/SOx standard?

Continuous data are the way to go for challenging models, looking at short-term effects and research purposes. Detection limits for current technology are on the order of 50-100 parts per trillion (ppt) or 0.13 ug/m3. My main concern with continuous measurements is that ambient concentrations are very low already and likely to drop even further in the next 5 years. As an example, average SO_2 in 2010 at the Yorkville, GA SEARCH site was 986 ppt. Hourly SO_2 concentrations were <100 ppt 15% of the time, <200 ppt 28% of the time, <500 ppt 50% of the time and <1000 ppt 68% of the time. Other rural sites in the SE (and maybe the NE) have even lower concentrations. To obtain meaningful data (short-term AND long-term averages) will require very careful management of instrument baseline. The figure below shows typical summertime SO_2 at YRK.



Charge Question 4: What are the panel's views on using existing NOy methods that are deployed, for example, in NCore as the measurement approach for NOy for the purpose of providing annual average values as an indicator for the NOx/SOx standard? What are the panel's views on EPA's assessment that additional study is needed before establishing an FRM based on the existing NOy methods? That is, are the methods already adequately demonstrated as a reference method to determine compliance with a NAAQS? What are the panel's views on the research plan for establishing existing NOy methods as an FRM?

Additional study is needed to establish an FRM for NO_y. Like SO_2, current NO_x analyzers are very sensitive, but it is not clear they are seeing or quantifying all NO_y components or to what extent there is interference from non- NO_y components (e.g., ammonia or particulate- NH_4). Extreme care is needed to ensure transmission of the more reactive components of NO_y into the catalytic converter and to monitor the efficiency of the converter. NCORE will be a very good test bed for NO_y measurements. Careful review of NCORE data will yield valuable insights into operational issues and resource requirements (e.g., what is the expected lifetime of a converter and is it possible to regenerate a converter?). Also, does it make sense to use NO for calibration purposes when the majority of NO_y in rural environments is NO_2 and higher?

Charge Question 5: What are the panel's views on using the emerging AMoN ammonia monitoring network that uses passive sampling technology as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?

Passive samplers can be used for 1-week or 2-week comparisons, but the model really needs to be tested on much shorter time scales (hourly or daily) to ensure the model has the processes right and to make source attribution inferences. The NO_y sites in Q8 should be equipped with NH_3 samplers or analyzers for higher time resolution measurements.

Charge Question 6: What are the panel's views on co-locating ammonia measurements at each location where the indictors are measured?

I strongly support this idea.

Charge Question 7: What are the Panel's views on using the CASTNET filter pack (FP) to measure ammonium ion as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?

The CASTNet filter pack should be modified to collect both ammonia and ammonium. This can be done by introducing a denuder (annular or honeycomb) upstream of the filter pack and an acid impregnated filter (citric or phosphorous) to the back of the FP.

Charge Question 8: What are the panel's views on establishing a suite of NOy species measurements at 2- 5 locations in different atmospheric and ecological regions for the purpose of evaluating air quality model and NOy instrument behavior?

I strongly support this idea. The more sites the better. Target components should be NO, photolytic NO_2, HNO_3 and PANs. Solid techniques for NO_2 and HNO_3 are in use by researchers in numerous part of the country. These can be adapted to more routine monitoring applications. Thermal-photolytic-chemiluminescent approaches to PANs should be explored.

Charge Question 9: What are the panel's views on utilizing the existing CASTNET and rural NCore networks as a starting infrastructure for the purpose of supporting the NOx/SOx standard?

This is a good starting point. However, I have some concerns that site locations and density will not adequately address variability in terrain, vegetation or source strength in areas of highest sensitivity. Reactive gases exhibit strong gradients between low elevation (valley) and high elevation (ridge) depending, in part, on sources within the valley. I am not sure these gradients can be represented by widely spaced CASTNet or NCORE sites.

Charge Question 10: What are the panel's views on using CASTNET filter pack (FP) to measure total nitrate (particulate nitrate plus nitric acid) as the measurement approach for the purpose of providing annual average values to support the NOx/SOx standard in diagnosing NOy instrument behavior and assist in delineating the relative fractions of contributing oxidized nitrogen species to total ambient oxidized nitrogen.

Simple modification of the CASTNet FP would greatly enhance is utility for the above purposes. As for ammonia, a KCl denuder ahead of the FP would capture HNO_3 while the downstream filters would collect particulate NO_3. There will still be confounding effects of coarse particulate NO_3, but at least this separates the gas phase from the particulate phase.

Charge Question 11: What are the panel's view of the broader consideration of using CASTNET, complemented by rural NCore, to serve as a framework for the nation's rural monitoring of important gases and aerosols in support of secondary standards and evaluating the behavior of regional air quality models?

As stated above, I think this is a reasonable start in a resource-constrained environment, but we need to take a hard look at techniques and siting. As noted by others, there are concerns about separation of monitoring responsibilities in CASTNET, which has traditionally been the bailiwick of the state and local agencies. The latter might be mitigated to some extent by enhanced auditing of CASTNET sites.

Comments from Mr. Henry (Dirk) Felton

Introduction:

The EPA should be commended for undertaking the very difficult challenge of designing the first multi-pollutant air quality standard. The standard should provide for a better understanding of the ecological impacts of air pollution on sensitive water bodies. One omission in the current design of the standard is any commitment to make measurements of water quality. Some regions of the country have relatively little water quality data which makes it difficult to evaluate the range of potential acidic indexes and the number of lakes in each region which are likely to be above or below a particular level. Water quality measurements at a minimum should include ANC and pH and should be collected so that the data is comparable from year to year. The change in the physical ecological indicator of ANC and pH over time will provide the necessary accountability for the modeling and monitoring approach used by the secondary standard and will also provide evidence to the public and other stakeholders that the program is providing real results.

The EPA's plan to designate modeled parameters that specify regional acid sensitivity to air pollutants as part of the NAAQS is problematic. These initially derived factors should be considered to be preliminary. The performance of the model factors in each region should be demonstrated and subject to change if new environmental data suggests that they can be improved. The EPA should allow the responsible State and Local monitoring agencies to either opt in or suggest alternate model parameters prior to the initial designations under this NAAQS. The EPA could then use a weight of evidence type of approach to consider which model parameters are appropriate for use in the first, and then for subsequent designations. This periodic check of model performance should also be expanded to include a comparison of the acidic index to representative lake water ANC.

Charge Question 1: What are the Panel's views on using the CASTNET filter pack (FP) to measure particulate sulfate for the purpose of providing annual average values as an indicator for the NOx/SOx standard? Given EPA plans primarily to document the capability of the CASTNET FP and develop the FRM for particulate sulfate based on the existing information and procedures, what are the Panel's views of this approach for setting the FRM?

This is an inexpensive and probably reasonable approach. The primary issue not resolved with this technique is the unknown collection and retention of larger particles. This could be significant in some eco-regions primarily in the western half of the country. The EPA should collocate this method with a low volume PM-10 in order to evaluate the retention of these particles by the CASTNET FP. There may be collocated data already available with CASTNET and IMPROVE PM-10.

Charge Question 2: What are the Panel's views on using the CASTNET filter pack (FP) to measure sulfur dioxide gas for the purpose of providing annual average values as an indicator for the NOx/SOx standard? If EPA would document the capability of the CASTNET FP and develops an FRM for sulfur dioxide gas based on the existing information and procedures, what are the Panel's view of this approach for setting the FRM?

A CASTNET filter pack or one of the commercially available passive alternatives is likely to be a reasonable alternative to the SO_2 FRM in these relatively clean environments. It would make sense to compare the CASTNET filter pack, the currently available passive samplers and the FRM in winter and summer months to see which is most effective and cost efficient for this network. It might be possible to overcome potential differences in the methods by using algorithms to adjust filter pack data to more closely emulate the FRM. This is easy to do since the Acidic Index is calculated on the past year's data and this will reduce the need to operate large numbers of FRMs in each eco-region. The data from one FRM can be used to adjust the data from multiple FEM filter packs within the same or similar eco-region.

Charge Question 3: What are the Panel's views on using the current primary FRM (high time resolution UVF) to measure sulfur dioxide gas for the purpose of providing annual average values as an indicator for the NOx/SOx standard?

The trace version of the SO2 FRM will work in these relatively pristine rural areas but the effort required to get accurate data at these extremely low concentrations may not be warranted. It is not clear that hourly SO_2 data is necessary at more than a handful of sites. Perhaps the rural NCore sites could provide the high frequency SO2 data that supplements a network that consists primarily of passive or filter pack sites. It would be appropriate to initiate the program with a less expensive passive SO_2 measurement and then require the FRM if it becomes apparent that the increased accuracy is needed.

The operation of the SO2 FRM may have to be modified to make it as accurate and stable as possible. The averaging time should be increased to 300 seconds to improve sensitivity and the quality and frequency of the zero adjustments must be increased. The automation of more frequent instrument zeros should be strongly encouraged.

A review of ambient SO_2 data collected with an FRM in the Adirondack Park region of New York State shows that for 2009 and 2010 data:

Site	Average (24-Hr data)	Max 24-Hr	Min 24-Hr
Piseco Lake	0.4 ppb	5.6 ppb	-0.2 ppb
Paul Smith's	0.6 ppb	4.5 ppb	0.0 ppb
Nick's Lake	0.6 ppb	5.3 ppb	-0.1 ppb
Whiteface Base	0.7 ppb	3.7 ppb	0.1 ppb

Site	Average (1-Hr data)	Max 1-Hr	Min 1-Hr
Piseco Lake	0.4 ppb	12.3 ppb	-0.3 ppb
Paul Smith's	0.6 ppb	9.9 ppb	-0.1 ppb
Nick's Lake	0.5 ppb	13.5 ppb	-0.1 ppb
Whiteface Base	0.7 ppb	17.5 ppb	-0.1 ppb

The average 2009 through 2010 SO_2 concentrations from the Piseco Lake site which is close to the center of New York's Adirondack Park is barely twice the detection limit of the commercially available trace level SO_2 monitor. One concern is that the relative error is quite large at these very low concentrations so the utility of the data to accurately discern one site from another within the same eco-region may be limited.

Charge Question 4: (a) What are the panel's views on using existing NOy methods that are deployed, for example, in NCore as the measurement approach for NOy for the purpose of providing annual average values as an indicator for the NOx/SOx standard?

The existing NOy method should be deployed but only in a limited number of sites. Unlike most of the other NAAQS in which an indicator is correlated with a health outcome, the proposed NOy indicator for this standard is being used to measure the sum of air concentrations that lead to a net deposition velocity. It is likely that only a few of the primary components of NOy (NO, NO_2, HNO_3, P-NO_3 and PAN) will be primarily responsible for nitrogen deposition in different regions of the country. This creates a great deal of uncertainty because the NOy measurement has not been fully characterized for each of these species in representative areas of the country and the resulting dataset may not be adequate to advance our understanding of what components are primarily responsible for the deposition or for future SIP development.

The current NOy method should be deployed at a handful of specific sites in areas of the country where different gas and aerosol compositions exist and where weather patterns are significantly different. The collection of this data is necessary in order to initiate model validation in comparison to ambient air and water quality data.

Charge Question 4: (b) What are the panel's views on EPA's assessment that additional study is needed before establishing an FRM based on the existing NOy methods? That is, are the methods already adequately demonstrated as a reference method to determine compliance with a NAAQS?

The EPA is correct that the NOy method needs additional evaluation before it should be considered to be eligible for FRM status. There are many issues that need to be addressed. The method must include a demonstration of conversion efficiencies for the expected suite of Nitrogen species in rural areas at all ambient and converter temperatures and with and without known interferences, a determination should be made of how long a converter lasts and if the converter efficiency changes over time for some species but not others, whether and what type of

bug screen should be installed, and a determination should be made on a species by species basis of optimum inlet height.

It is advisable to optimize the method and to thoroughly document the recommendations prior to considering the method for FRM designation. Once an analyzer is designated as an FRM, it is more difficult to make needed changes.

Charge Question 4: (c) What are the panel's views on the research plan for establishing existing NOy methods as an FRM? [Note suggested improvement to the plan would be appreciated, particularly ones that would help complete the study on time.]

The EPA's research plan must be thorough and provide ample time for laboratory evaluation and for field demonstration. The ambient field demonstrations must include locations that encompass a wide range of gas and aerosol compositions including known interferents as well as a range of operator experience. Utilizing one site will not meet this need. Some of the issues that have come out of the preliminary NCore NOy operation have included questions about cold weather calibration, sample residence time between the converter and the analyzer and whether the transfer lines should be shielded from light. None of these are addressed in the research plan.

The EPA must resist the urge to quickly designate an FRM for NOy. The current method may or may not meet the intended data need and the designation of a poorly performing FRM will harm the ability of monitoring agencies to collect this data in the future.

Charge Question 5: What are the panel's views on using the emerging AMoN ammonia monitoring network that uses passive sampling technology as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?

The AMoN monitoring technology is promising and it should be considered for use during the initial deployment of the NOx/SOx monitoring program. The inexpensive nature and ease of deployment of this method are a tremendous benefit. The method can be deployed in its current state to determine spatial gradients within an eco-region continuously or on an as needed basis. The accuracy and precision of the method must be defined in representative regions and climates before the data from the method can be accepted at face value for use in model verification.

Charge Question 6: What are the panel's views on co-locating ammonia measurements at each location where the indictors are measured?

There must be enough monitors to reasonably describe the variation in ammonia concentration across each of the eco-regions. This variability in ammonia concentrations over the period of the integrated samples for this network that encompasses mountainous rural areas and coastal plains

is unknown. It would be advantageous to conduct a thorough review of the data collected in the first year to determine the adequacy of the network for each of the monitored species including ammonia. An analysis of the inter-site ammonia variability in relatively uniform eco-regions compared to the variability in non-uniform eco-regions should help. Emphasis should be placed on measurements in eco-regions with data indicating that they are near the level of the standard. These are the areas that will need the highest density of measurements of the indicators as well as for parameters necessary for model evaluation such as ammonia.

Charge Question 8: What are the panel's views on establishing a suite of NOy species measurements at 2- 5 locations in different atmospheric and ecological regions for the purpose of evaluating air quality model and NOy instrument behavior?

This is certainly a good idea and is quite necessary so that the significance of the NOy measurement can be fully understood chemically, geographically and seasonally. The individual species measurements are difficult, expensive and not at all straightforward to make so they should be restricted to just a few locations. The EPA should not expect all monitoring agencies to be capable of operating these complex and research grade instruments. The EPA may want to partner with other state, local and federal monitoring agencies and academic researchers who have experience making these measurements and can accomplish them in selected eco-regions.

Charge Question 9: What are the panel's views on utilizing the existing CASTNET and rural NCore networks as a starting infrastructure for the purpose of supporting the NOx/SOx standard?

In general, neither the existing CASTNET nor rural NCore monitoring networks are suitable alone. Leveraging existing networks is certainly less expensive than initiating new sites but the first step must be to identify the appropriate infrastructure for monitoring in support of this standard. Then the existing CASTNET, rural NCore, rural State and Local monitoring agency sites and IMPROVE sites can be evaluated in comparison to what is needed for each eco-region. In some eco-regions, such as in the south-east there may be enough suitably located State and Local monitoring agency sites and CASTNET sites to provide a monitoring infrastructure to support this standard. In most of the other eco-regions there are fewer CASTNET sites and more State and Local monitoring agency and IMPROVE sites. Consideration should be given to relocating a rural NCore site to meet NCore and NOx/SOx monitoring objectives if the expenses in such a move are less than the cost of establishing another stand-alone site. One advantage to considering this now is that the NCore sites are new and do not have a long data record.

The necessary infrastructure for the initial deployment of this network for each of the large eco-regions should include a water quality monitoring program, one well instrumented site that could be an NCore type of sites as well as a few passive satellite monitors that provide a subset of measurements in areas of the region where air concentrations are expected to differ. The sites should be located so that they are representative of air quality in areas that are:

1. Near moderately impacted water bodies: Severely impacted water bodies may not show improved ANC due to air quality improvements over the time scale of the next NAAQS review due to other considerations such as local geology. Water bodies with minor ANC degradation may show improvements that are too small to detect over the interval between NAAQS reviews.

2. Away from significant point sources and eco-region boundaries: The sites should represent as large an area with reasonably uniform air quality as possible.

The satellite sites should be selected to help discern how large an area the central eco-region monitor actually represents. Altitude, proximity to upwind sources and meteorological patterns affected by valleys and upslope or downslope conditions will all reduce the representativeness of central site measurements. The subset of parameters monitored at the satellite sites should be selected because they significantly contribute to model uncertainty due to changes in air quality over the eco-region.

One way to economically provide high spatial resolution data is to periodically carry out additional passive or CASTNET filter pack monitoring at multiple locations within an eco-region for 1-2 consecutive weeks. This might have to be done 2-4 times a year to provide enough temporal data to validate the model parameters specific to this region. The extra monitoring resources should be targeted for regions that may be close to the acidic index value selected for the standard. This extra spatial information could also help characterize the non-uniform eco-regions that have large differences in precipitation, terrain features including valleys and other elevation changes and significant sources.

Charge Question 10: What are the panel's views on using CASTNET filter pack (FP) to measure total nitrate (particulate nitrate plus nitric acid) as the measurement approach for the purpose of providing annual average values to support the NOx/SOx standard in diagnosing NOy instrument behavior and assist in delineating the relative fractions of contributing oxidized nitrogen species to total ambient oxidized nitrogen.

There are ways to modify the filter pack to separate the nitrate and nitric acid for separate analysis but this would necessitate a change in the design of the filter pack. This will work but it will make the data incompatible with other monitoring objectives such as consistency with the rest of the CASTNET monitoring network. It is far simpler and fairly inexpensive to utilize a

standalone filter and denuder combination for nitrate and nitric acid at a subset of sites where this measurement is needed. This would necessitate the installation of another flow channel but that would provide the broadest utility for the data.

Charge Question 11: What are the panel's view of the broader consideration of using CASTNET, complemented by rural NCore, to serve as a framework for the nation's rural monitoring of important gases and aerosols in support of secondary standards and evaluating the behavior of regional air quality models?

Some State and Local monitoring agencies are not going to be comfortable with CASTNET assuming a role in monitoring for comparison to a NAAQS. CASTNET management has not demonstrated concern with State and Local monitoring agency objectives and in fact has been counterproductive in some instances. The use of a for-profit contractor for the collection of long term data is not likely to remain viable. Additionally, monitoring agencies need to have the flexibility to add sites or parameters as needed to address future modeling uncertainties and eventually to address options for SIPs.

It is likely that some of the CASTNET measurement methods may be appropriate for use in the secondary NOx/SOx monitoring network. These methods should be made available on a national contract basis similar to the way the air toxics analyses can be obtained for the EPA NATTs program. This will permit monitoring agencies to utilize these methods at any of the existing or new monitoring sites that are selected for this network.

Comments from Dr. Philip Hopke

It is somewhat difficult to respond to the charge questions since the form and ranges of the levels of a proposed secondary standard are not clear in Chapter 2 of the PA, the only chapter sent to us. Tuesday's discussions by the panel will be very helpful in setting the context in which measurements are needed. I will attempt to address the questions related to ammonia measurements as it is difficult to discuss the value of collocating a sampler without some background on the samplers themselves. Thus, I will address the following questions:

Charge Question 6. What are the panel's views on using the emerging AMoN ammonia monitoring network that uses passive sampling technology as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?

Charge Question 7. What are the panel's views on co-locating ammonia measurements at each location where the indictors are measured?

Charge Question 8. What are the Panel's views on using the CASTNET filter pack (FP) to measure ammonium ion as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?

It should be noted that these are numbered differently in the Charge Questions memo from that in the Draft Agenda.

Response to Charge Question 6

Although the NADP has been using these samplers since November 2007 at multiple stations, I was unable to find comparison or evaluation data. The initial studies appear to show that the sampler had adequate precision and accuracy for making such measurements, but it is not clear what the field experience has been. It would have been helpful if some evaluative material had been provided. Given that they said that "The National Atmospheric Deposition Program will evaluate all of the results, and consider whether this special study will become a full standing network within the NADP system. This decision should be considered in the Winter, 2009" and it is now 2011, one would have hoped for documentation since from the data that can be downloaded from the NADP site, they have continued to collect samples through at least last summer. Thus, it is somewhat difficult to fully assess the success of the AMoN trials of the diffusion sampler. The precision values that were available looked good, but there was no obvious accuracy data that I could find. Thus, there has been inadequate information provided to permit us to assess the AMoN effort.

Response to Charge Question 7

It is clearly highly advantageous to have good ammonia data at every station if there are appropriate integrating monitors available with sufficient accuracy and precision. There needs to be a DQO effort to define how good the ammonia has to be to permit ion balances to be adequately estimated from the set of measured species. As the principal basic gas in the atmosphere, it is important to have better data on the concentrations and spatial variation across the US.

Response to Charge Question 8

Clearly the CASNET filter pack can be modified to have a citric acid impregnated filter in the FP along with the base-treated filter to get the acid gases. There is a potential problem of volatilization of ammonia from the initial filter that collects the particulate ammonium nitrate that could lead to an overestimated value of gaseous ammonia. It would seem sensible to do a side-by-side comparison between the AMoN diffusion sampler against another filter in the CASNET FP. Then through a DQO process, the performance and cost of the samplers can be assessed and an appropriate choice made.

Additional Comments on NADP Ammonia Measurements

I talked to David Gray of the NADP program about their AMoN experience. They tested Ogawa badges, the UK ALPHA sample (see website information noted below), the Radiello sample, and a standard denuder sampler. They deployed three samplers of each type for 2 week periods. They found poor precision with the Ogawa badge and dropped them earlier in the study. The Radiello sampler was very simple to use, very hard to contaminate, but somewhat more expensive. The UK sampler also showed good precision and was less expensive, but was a bit more likely to be contaminated if not handled carefully. They are in the final stages of preparing a manuscript to submit for publication at which time he will share the submitted version.

UK ALPHA sample website information regarding the UK's Methodologies for Measuring Ammonia, Trace Gases and Aerosols - Measuring Concentrations of Atmospheric Trace gases and aerosols, is found at the following website address:
http://www.uk-pollutantdeposition.ceh.ac.uk/ammonia_methodology

Information on the NADP program, AMoN activities can be found off the following USEPA website: http://www.epa.gov/castnet/javaweb/docs/flyer_AMoN.pdf

Comments from Dr. Rudolf Husar

Charge Question 1: What are the Panel's views on using the CASTNET filter pack (FP) to measure particulate sulfate for the purpose of providing annual average values as an indicator for the NOx/SOx standard? Given EPA plans primarily to document the capability of the CASTNET FP and develop the FRM for particulate sulfate based on the existing information and procedures, what are the Panel's views of this approach for setting the FRM?

CASTNET FP should be appropriate for the annual average sulfate. If the CASTNET PF is certified as FRM, does it mean that sulfate from IMPROVE/STN would not be used in estimating the sulfur indicator? If so, why not use these long-term, robust multi-use networks?

Charge Question 3: What are the Panel's views on using the current primary FRM (high time resolution UVF) to measure sulfur dioxide gas for the purpose of providing annual average values as an indicator for the NOx/SOx standard?

I strongly recommend high time resolution SO_2 at rural sites, particularly for model evaluation/calibration. The highly variable SO_2 concentration over rural regions along with extensive SO_4 data from IMPROVE/STN is the best index for evaluating the (important and highly uncertain) sulfur dry deposition in the model.

Charge Question 4: What are the panel's views on using existing NOy methods that are deployed, for example, in NCore as the measurement approach for NOy for the purpose of providing annual average values as an indicator for the NOx/SOx standard? What are the panel's views on EPA's assessment that additional study is needed before establishing an FRM based on the existing NOy methods? That is, are the methods already adequately demonstrated as a reference method to determine compliance with a NAAQS? What are the panel's views on the research plan for establishing existing NOy methods as an FRM? [Note suggested improvement to the plan would be appreciated, particularly ones that would help complete the study on time.]

I am not qualified to comment on the NO_y measurement.

Charge Question 5: What are the panel's views on using the emerging AMoN ammonia monitoring network that uses passive sampling technology as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?

Not familiar with the AMoN network

Charge Question 6: What are the panel's views on co-locating ammonia measurements at each location where the indictors are measured?

In general, co-location of different measurements is desirable since it enhances the context of the air quality characterization. However, for the proposed standard, ammonia is to be provided by the CMAQ model, not from observations. Accordingly, the primary use of the ammonia measurements is linked to the model: e.g. verification of ammonia emissions, spatial and seasonal pattern, information about deposition and chemical reactions, etc. The indicator measurements for NO_y, SO_x are receptor-oriented at the eco-regions.

Hence, for optimal network design the ammonia-for-model and the indicator-for-AAI may lead to different configuration, e.g. higher ammonia monitoring density in the Upper Midwest.

Charge Question 7: What are the Panel's views on using the CASTNET filter pack (FP) to measure ammonium ion as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?

Given that the pattern of ambient ammonia is both cyclic (diurnal) and episodic, ammonia measurements should be at higher time resolution to discern these variations and to compare them with the model.

Charge Question 8: What are the panel's views on establishing a suite of NOy species measurements at 2- 5 locations in different atmospheric and ecological regions for the purpose of evaluating air quality model and NOy instrument behavior?

Measuring the complete NO_y mix at a few characteristic locations is a terrific idea. As much as possible, those 'super sites' should also contain other observations that would increase the width of the pollutant characterization.

Charge Question 9: What are the panel's views on utilizing the existing CASTNET and rural NCore network as a starting infrastructure for the purpose of supporting the NOx/SOx standard?

No one should ignore both existing networks and start a brand new one, since CASTNET and NCore are not exactly what is the perceived need now. (just kidding!). Of course one should reuse existing networks end begin integrating the observations arising from these existing and persistent networks, regardless of their respective 'original' purpose.

Actually I would ask why are the IMPROVE/STN and the NADP not included in the pool of

relevant measurements? They are not 'FRM'? They are NIH?

Charge Question 10: What are the panel's views on using CASTNET filter pack (FP) to measure total nitrate (particulate nitrate plus nitric acid) as the measurement approach for the purpose of providing annual average values to support the NOx/SOx standard in diagnosing NOy instrument behavior and assist in delineating the relative fractions of contributing oxidized nitrogen species to total ambient oxidized nitrogen.

I am not qualified to comment on total nitrate measurement.

Comments from Dr. Daniel Jacob

Charge Question 1: What are the Panel's views on using the CASTNET filter pack (FP) to measure particulate sulfate for the purpose of providing annual average values as an indicator for the NOx/SOx standard? Given EPA plans primarily to document the capability of the CASTNET FP and develop the FRM for particulate sulfate based on the existing information and procedures, what are the Panel's views of this approach for setting the FRM?

I think that it is an appropriate method. The FP is a well-established method for reliable sulfate measurements. Weekly temporal resolution is fine – higher would be overkill. The CASTNET FP only measures the <2.5um fine fraction, and the coarser fraction makes a significant contribution to sulfate deposition. However, using a measurement integrating all sizes would just complicate interpretation of the relative contribution of coarse vs. fine in the measurement. Better to just measure the fine fraction and use a model- or observation-derived correction factor to add the relevant contribution of the coarse fraction (excluding sea salt and soil dust).

Charge Question 2: What are the Panel's views on using the CASTNET filter pack (FP) to measure sulfur dioxide gas for the purpose of providing annual average values as an indicator for the NOx/SOx standard? If EPA would document the capability of the CASTNET FP and develops an FRM for sulfur dioxide gas based on the existing information and procedures, what are the Panel's view of this approach for setting the FRM?

An issue with SO_2 is the large diurnal variation that correlates with deposition velocity. The diurnal amplitude for SO_2 is much larger than for sulfate and matters more since SO_2 makes a much bigger contribution to SO_x dry deposition than sulfate. This complicates the interpretation of weekly measurements. Hourly measurement by the primary FRM would be much better. If cost is an issue with using the primary FRM, then perhaps the primary FRM could be used to inform the general diurnal pattern of SO_2 concentrations needed to interpret the weekly measurements.

Charge Question 3: What are the Panel's views on using the current primary FRM (high time resolution UVF) to measure sulfur dioxide gas for the purpose of providing annual average values as an indicator for the NOx/SOx standard?

I think that this would be much better than the FP because the hourly resolution is important for SO_2 (cf. comment on question 2).

Charge Question 4: What are the panel's views on using existing NOy methods that are deployed, for example, in NCore as the measurement approach for NOy for the purpose of providing annual average values as an indicator for the NOx/SOx standard? What are the panel's views on EPA's assessment that additional study is needed before establishing an FRM based on the existing NOy methods? That is, are the methods already adequately demonstrated as a reference method to determine compliance with a NAAQS? What are the panel's views on the research plan for establishing existing NOy methods as an FRM? [Note suggested improvement to the plan would be appreciated, particularly ones that would help complete the study on time.]

Instruments to measure total NO_y have been compared successfully in the past to the sum of measurements of individual species. This is amply documented in the literature. However, the NO_y measurement is finicky on a number of accounts: (1) inlet losses for HNO_3, (2) particle size cut for nitrate, (3) positive interference from reduced N species. Because of this, EPA should be very prudent before selecting a FRM. The HEASD plan for establishing the FRM reliability of NO_y measurement methods seems reasonable. I recommend that validation campaigns be done for both summer and winter because of the change in NO_y speciation. There is a lot of expertise in the research community in testing the reliability of NO_y instruments and I recommend that David D. Parrish (NOAA/ESRL) be asked to comment on the HEASD plan. The NOAA/ESRL lab has considerable expertise that could be tapped in advising EPA on high-quality measurements of NO_y species and total NO_y. The research community also conducts regular intensive campaigns at surface sites measuring a suite of NO_y species as well as total NO_y (Harvard Forest in Massachusetts, PROPHET in Michigan, Niwot Ridge in Colorado, Blodgett Forest in California come to mind). It may be advisable to test the NO_y instrument considered as FRM as part of these campaigns.

Charge Question 5: What are the panel's views on using the emerging AMoN ammonia monitoring network that uses passive sampling technology as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?

I have no expertise on the quality of the measurement. My understanding is that it would have weekly resolution, which I would find difficult to interpret in the absence of information on diurnal variations in ammonia. I would expect these diurnal variations to be large and complex depending on whether the local area is a significant ammonia source or not.

Charge Question 6: What are the panel's views on co-locating ammonia measurements at each location where the indictors are measured?

That seems like a good idea considering the importance of model-derived L(NHx) in setting the standard. One should being able to evaluate the model ammonia at the locations where compliance with the standard is determined.

Charge Question 7: What are the Panel's views on using the CASTNET filter pack (FP) to measure ammonium ion as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?

FP ammonium measurements are subject to condensation/volatilization biases. In addition, ammonium concentrations do not provide a good test of model ammonia because under acid-neutralized conditions they are actually determined by the supply of sulfate and nitrate. I think that it would be a better idea to have a FP measurement of total ammonia+ammonium (NH_x), which would be more reliable and more useful to test model ammonia sources.

Charge Question 8: What are the panel's views on establishing a suite of NOy species measurements at 2- 5 locations in different atmospheric and ecological regions for the purpose of evaluating air quality model and NOy instrument behavior?

Once the reliability of the NO_y instrument has been established (HEASD proposal) I don't see much point in continuing to evaluate its behavior. Measuring NO_y speciation is very important for evaluating air quality models but this is already done at some research sites (see comment 4). The EPA might consider coordinating with researchers at these sites. The research sites are mainly in relatively remote areas and the EPA might consider focusing on more polluted sites, such as the Supersites.

Charge Question 9: What are the panel's views on utilizing the existing CASTNET and rural NCore networks as a starting infrastructure for the purpose of supporting the NOx/SOx standard?

Existing sites should be used as much as possible but may not provide the coverage necessary, for example in the upper Midwest. It seems to me that the geographical monitoring needs for the NO_x / SO_x standard should first be determined independently, and then leveraged against existing sites.

Charge Question 10: What are the panel's views on using CASTNET filter pack (FP) to measure total nitrate (particulate nitrate plus nitric acid) as the measurement approach for the purpose of providing annual average values to support the NOx/SOx standard in diagnosing NOy

instrument behavior and assist in delineating the relative fractions of contributing oxidized nitrogen species to total ambient oxidized nitrogen.

To my knowledge the FP method can measure total nitrate very reliably. From the standpoint of deriving a dry deposition flux, however, it makes of course tremendous difference whether that nitrate is present as HNO_3 or particulate nitrate. But that is a general issue with the use of unspeciated measurements to infer a NO_y dry deposition flux. There are very strong vertical gradients of HNO_3 in the lower few tens of meters, so that a having a standard above-canopy altitude is essential for all measurements in the network.

What would really help are FP measurements of speciated HNO_3 and aerosol nitrate, rather than total nitrate. These are available from CASTNET. See comment 5.

Charge Question 11: What are the panel's view of the broader consideration of using CASTNET, complemented by rural NCore, to serve as a framework for the nation's rural monitoring of important gases and aerosols in support of secondary standards and evaluating the behavior of regional air quality models?

These are great sites for evaluating air quality models because they are generally not affected by local (and often fluctuating) sources for which models may have little simulation capability. The flip side of course is that they do not provide information for areas most likely to be affected by excessive deposition.

Comments from Dr. Peter H. McMurry

(NOTE: I have not provided answers to questions that were not assigned to me and for which other Committee members have more authoritative first-hand experience. I have read the preliminary comments that were posted on line on 2/11/11, and I think many good points have been made.)

Charge Question 1: What are the Panel's views on using the CASTNET filter pack (FP) to measure particulate sulfate for the purpose of providing annual average values as an indicator for the NOx/SOx standard? Given EPA plans primarily to document the capability of the CASTNET FP and develop the FRM for particulate sulfate based on the existing information and procedures, what are the Panel's views of this approach for setting the FRM?

I wonder if it might not be preferable to use a sampler with a 2.5 µm inlet to ensure compatibility with data from other networks? Also, do model predictions of sulfates focus largely on fine particulate sulfate? If so, then measurements carried out with a 2.5 µm cut would ensure fidelity between models and measurements. I believe this is an important consideration if the sampling and analytical uncertainties for sulfates are smaller than the incremental sulfate associated with coarse particles.

Charge Question 2: What are the Panel's views on using the CASTNET filter pack (FP) to measure sulfur dioxide gas for the purpose of providing annual average values as an indicator for the NOx/SOx standard? If EPA would document the capability of the CASTNET FP and develops an FRM for sulfur dioxide gas based on the existing information and procedures, what are the Panel's views of this approach for setting the FRM?

If long term measurements have verified that FP SP2 provides an accurate measurement of the annual average, then I think this is a cost-effective solution to meeting this objective.

Charge Question 3: What are the Panel's views on using the current primary FRM (high time resolution UVF) to measure sulfur dioxide gas for the purpose of providing annual average values as an indicator for the NOx/SOx standard?

As was pointed out by a Committee Member, average SO_2 concentrations at some locations may be only slightly above the minimum detection level for UVF SO_2 monitors. If such cases, the UVF SO_2 monitor would not provide accurate annual average values, although it presumably could show that annual average values were well below requirements of the standard. Is there the potential that a passive sampler could provide more accurate long-term average values? If so, this would be a more cost-effective solution.

Charge Question 4(a) What are the panel's views on using existing NOy methods that are deployed, for example, in NCore as the measurement approach for NOy for the purpose of providing annual average values as an indicator for the NOx/SOx standard?

Charge Question 4(b) What are the panel's views on EPA's assessment that additional study is needed before establishing an FRM based on the existing NOy methods? That is, are the methods already adequately demonstrated as a reference method to determine compliance with a NAAQS?

It seems clear to me that more work needs to be done to establish capabilities and limitations of the NO_y instruments before they are set as FRMs.

Charge Question 4(c) What are the panel's views on the research plan for establishing existing NOy methods as an FRM? [Note suggested improvement to the plan would be appreciated, particularly ones that would help complete the study on time.]

I like the use of the VOAG for producing particulate nitrate samples at known concentrations. Although this can be tricky experimentally, it has the potential to produce aerosols with nitrate concentrations that are accurately known from first principles. The first principles measurement is possible because measurements are done with monodisperse particles. Since, in principle, the nitrate mass in each droplet produced by the VOAG is known, the total mass of nitrate collected is determined by the number of droplets collected (droplet concentration X flowrate X sampling time X nitrate mass per droplet) of nitrates in each droplet. Also, these measurements will be carried out with relatively large particles (>0.5 µm), so will provide a more stringent test of the apparatus than would occur if experiments were done with a polydisperse aerosol. I believe the HEASD team ought to be able to do this work well, as members of the team have extensive experience with the VOAG.

Charge Question 5: What are the panel's views on using the emerging AMoN ammonia monitoring network that uses passive sampling technology as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?

OK if prior QA work has been published in peer-reviewed journal articles.

Charge Question 6: What are the panel's views on co-locating ammonia measurements at each location where the indictors are measured?

Co-located measurements of ammonia at each sampling location would seem to be very important.

Charge Question 7: What are the Panel's views on using the CASTNET filter pack (FP) to measure ammonium ion as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?

Charge Question 8: What are the panel's views on establishing a suite of NOy species measurements at 2- 5 locations in different atmospheric and ecological regions for the purpose of evaluating air quality model and NOy instrument behavior?

I think it would be a good idea to deploy exploratory speciated NO_y measurements at a limited number of locations. This will facilitate model refinement, and will also allow the measurement methods to be evaluated and refined.

Charge Question 9: What are the panel's views on utilizing the existing CASTNET and rural NCore networks as a starting infrastructure for the purpose of supporting the NOx/SOx standard?

My initial reaction to this proposal was, "why not?" I think Dirk Felton's comments show clearly why it is essential to include input from state and local agencies in these Committees. I defer to Dirk.

Charge Question 11: What are the panel's view of the broader consideration of using CASTNET, complemented by rural NCore, to serve as a framework for the nation's rural monitoring of important gases and aerosols in support of secondary standards and evaluating the behavior of regional air quality models?

Again, I defer to Dirk Felton on this point. His personal experience with these networks provides an important perspective that requires consideration. I do not have similar experience.

Comments from Dr. Allen Robinson

Charge Question 1: What are the Panel's views on using the CASTNET filter pack (FP) to measure particulate sulfate for the purpose of providing annual average values as an indicator for the NOx/SOx standard? Given EPA plans primarily to document the capability of the CASTNET FP and develop the FRM for particulate sulfate based on the existing information and procedures, what are the Panel's views of this approach for setting the FRM?

The CASTNET FP is one of several well-established techniques for measuring particulate sulfate. Presumably the suite of established techniques should be considered when setting an FRM. The major difference between CASTNET and other existing techniques seems to be size cut -- open face versus PM2.5. Although the CASTNET FP is open faced, how well has its collection efficiency for coarse PM been characterized? Quantitative collection of coarse PM requires careful inlet design. There may be some advantages with using a FP with a more precisely defined cut point. There may also be some advantages to trying to better utilize the data of IMPROVE and other existing networks.

Charge Question 2: What are the Panel's views on using the CASTNET filter pack (FP) to measure sulfur dioxide gas for the purpose of providing annual average values as an indicator for the NOx/SOx standard? If EPA would document the capability of the CASTNET FP and develops an FRM for sulfur dioxide gas based on the existing information and procedures, what are the Panel's view of this approach for setting the FRM?

The CASTNET filter pack (FP) and other filter pack based approaches are widely deployed and well established techniques for measuring SO_2 gas concentrations in rural areas with low levels (less than 5 ppbv). In fact, the greater sensitivity of FP based techniques may offer some advantages at lower concentration than continuous monitors. Therefore, I think it is appropriate to consider the CASTNET FP as the basis for measuring SO_2 gas as an indicator for the NO_x / SO_x standard. However, the performance of the CATNET FP compared to the existing SO_2 FRM at low level found in rural areas needs to be well documented.

Scientifically continuous monitors will provide a lot of extra information for model evaluation, etc.

Charge Question 3: What are the Panel's views on using the current primary FRM (high time resolution UVF) to measure sulfur dioxide gas for the purpose of providing annual average values as an indicator for the NOx/SOx standard?

An advantage using the current primary FRM for evaluating the NO_x / SO_x standard is that hourly data can be used for model evaluation. Therefore, all else being equal (cost and

performance), collecting more high time resolved data seems beneficial. However, running trace SO_2 monitors in rural areas is challenging, requiring careful attention to zero offsets and other QA/QC measurements. At a minimum, continuous monitors should be run at a subset of sites to provide data for model evaluation.

Charge Question 4: What are the panel's views on using existing NOy methods that are deployed, for example, in NCore as the measurement approach for NOy for the purpose of providing annual average values as an indicator for the NOx/SOx standard? What are the panel's views on EPA's assessment that additional study is needed before establishing an FRM based on the existing NOy methods? That is, are the methods already adequately demonstrated as a reference method to determine compliance with a NAAQS? What are the panel's views on the research plan for establishing existing NOy methods as an FRM? [Note suggested improvement to the plan would be appreciated, particularly ones that would help complete the study on time.]

There are a number of commercially available instruments for measuring NO_y. My perception (e.g. Luke et al. AE 2010) is that these instruments can provide high quality data in a research environment. However, the performance in a compliance monitoring context (less well trained technicians, etc.) needs to be evaluated. For the NO_x / SO_x standard understanding their performance at low concentration, rural conditions will be essential.

I agree with the Agency's view that additional study is needed before establishing a NO_y FRM. I would characterize it as substantial additional study from an instrument demonstration perspective, not instrument development perspective. Key issues include conversion efficiency of catalyst for the suite of NO_y species and inlet performance for different species. These issues must be addressed before designating an FRM.

A shortcoming of the research plan was that all of the ambient measurements used in the evaluation study are going to be made in NC. There are two issues. One is to test the instrument across a wide range of climatic conditions (i.e. cold winter weather); for example, by making winter time measurements at sites in the Northeast and Upper Midwest. In addition, more thinking needs to be done about testing the instruments in a broader range of atmospheric conditions (beyond climatic conditions). The EPA should considering partnering with other measurement campaigns by NOAA and other organizations when making these measurements.

Charge Question 5: What are the panel's views on using the emerging AMoN ammonia monitoring network that uses passive sampling technology as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?

More ammonia data are desperately needed for model evaluation and understanding the

effectiveness of potential control strategies. I have not seen peer-reviewed evaluation of this sampler, but results in the grey literature suggest that it appears promising.

Charge Question 6: What are the panel's views on co-locating ammonia measurements at each location where the indicators are measured?

Co-locating samplers would be ideal but probably not feasible given resource constraints. Certainly co-locating at a suitable set of sites that span range of atmospheric conditions is needed. These would be core sites with a more comprehensive set of instruments used to support model evaluation and investigation of atmospheric processes.

Charge Question 7: What are the Panel's views on using the CASTNET filter pack (FP) to measure ammonium ion as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?

More data are needed for model evaluation. However, ammonium ion measurements by themselves have pretty limited value in evaluating emissions inventories, models, and especially the critical questions of: when are we in potential sulfate-nitrate substitution regimes and when is NH_3 the limiting reagent (see e.g. Pinder et al. JGR 2006)? Therefore, if the data are being primarily collected for model evaluation there may be a more efficient use of funds.

NH_3 (g) and/or total NHx are much more useful. NHx total *or* NH_3 (g) plus NH_4+ is the best case scenario. NH_3 (g) is probably more useful than NH_4+ (if there is enough free ammonia in the gas-phase, you can deduce that the sulfate is neutralized). NH_4+ by itself is probably the least useful. NHx is probably the easiest to measure so that would be the best.

On all of these, time resolution is important for model evaluation. The inorganic thermo regime bounces around enough that you want to be able to see that. Also, the higher time resolution instruments are naturally less vulnerable to various positive/negative partitioning artifacts for NH_4+. Daily is probably decent. Hourly would be ideal. Multi-day exposures are probably not very helpful. “One in six” is better than multi-day exposures.

Charge Question 8: What are the panel's views on establishing a suite of NOy species measurements at 2- 5 locations in different atmospheric and ecological regions for the purpose of evaluating air quality model and NOy instrument behavior?

I strongly support this idea. It seems like evaluating the NO_y instrument behavior in this fashion should be done before designating an FRM method. I.e. This should be part of EPA’s research plan.

Charge Question 9: What are the panel's views on utilizing the existing CASTNET and rural NCore networks as a starting infrastructure for the purpose of supporting the NOx/SOx standard?

Leveraging existing networks seems sensible, cost-effective starting point. However, EPA first must independently define the selection criteria for sites to evaluate the new secondary SO_x / NO_x NAAQS. Once these selection criteria are defined, EPA can then determine how many of the CASTNET and NCore sites are suitable for evaluating the new standard and how many new sites will need to be established. Presumably some new sites would need to be established.

Charge Question 10: What are the panel's views on using CASTNET filter pack (FP) to measure total nitrate (particulate nitrate plus nitric acid) as the measurement approach for the purpose of providing annual average values to support the NOx/SOx standard in diagnosing NOy instrument behavior and assist in delineating the relative fractions of contributing oxidized nitrogen species to total ambient oxidized nitrogen.

The sum of the Teflon and Nylon nitrate data collected using CASTNET FP provides a reasonable measure of the sum of nitric acid, nitrous acid, and ammonium nitrate. For a total nitrate FRM, an acid gas denuder should be used upstream of the Nylon filter. If EPA documents the capability of the CASTNET FP using existing data and additional studies, then it would be appropriate to consider it as an FRM.

A FP measure of annual average values to support the NO_x / SO_x standard is reasonable. However, these measurements will have very limited value for evaluating a NO_y instrument that provides much higher time resolved data.

Charge Question 11: What are the panel's view of the broader consideration of using CASTNET, complemented by rural NCore, to serve as a framework for the nation's rural monitoring of important gases and aerosols in support of secondary standards and evaluating the behavior of regional air quality models?

See answer to #10.

Comments from Dr. Jay Turner

I applaud the Agency for taking a holistic, multimedia approach that includes a form of the standard grounded in a water quality metrics with ambient air concentrations as indicators that are inputs to the calculation of the water quality metric. This also provides a challenge in responding to the charge questions in that it is not clear what MQOs/DQOs are appropriate for the ambient air measurements. This general comment is reflected in the cursory preliminary responses provided below. In most cases, it is difficult to assess whether a given measurement method is appropriate in the absence of information about concentration ranges of interest, desired precision and accuracy, and so on.

Charge Question 1: What are the Panel's views on using the CASTNET filter pack (FP) to measure particulate sulfate for the purpose of providing annual average values as an indicator for the NOx/SOx standard? Given EPA plans primarily to document the capability of the CASTNET FP and develop the FRM for particulate sulfate based on the existing information and procedures, what are the Panel's views of this approach for setting the FRM?

As noted in the background documents, the CASTNET filter has the advantage of being an open sampler that will collect particles larger than 2.5 □m. While most of the sulfate is expected to be in the fine fraction, in many cases there will be some sulfate mass in the supermicron fraction and these particles would have high deposition velocities. The goal of capturing the sulfate mass of these particles is understood, but assumptions would still need to be made about the particle size distributions and in the absence of such site-specific information it is not clear to me that the open sampler design brings added value. That said, the CASTET filter pack might be an appropriate FRM pending the outcomes of the planned effort to document the sampler's capability and a clearer articulation of the measurement quality objectives.

Charge Question 2: What are the Panel's views on using the CASTNET filter pack (FP) to measure sulfur dioxide gas for the purpose of providing annual average values as an indicator for the NOx/SOx standard? If EPA would document the capability of the CASTNET FP and develops an FRM for sulfur dioxide gas based on the existing information and procedures, what are the Panel's views of this approach for setting the FRM?

Again, the key issue is whether the CASTNET FP meets the data quality objectives which have not yet been defined. The provided background documents mentioned that the CASTNET measurements are generally accepted to be high quality, but this is a subjective statement. What data are available to compare the CASTNET filter pack SO_2 to other measurement methods? CASTNET includes two collocated sites; what information is available about the collocated precision?

Charge Question 3: What are the Panel's views on using the current primary FRM (high time resolution UVF) to measure sulfur dioxide gas for the purpose of providing annual average values as an indicator for the NOx/SOx standard?

The ultraviolet fluorescence (UVF) method is an FRM for the current primary SO_2 NAAQS. As such it has been deemed acceptable for compliance monitoring for a 0.030 ppmv annual average standard. Performance specifications candidate reference and equivalent methods are documented in 75 FR 35597- 35601. In the context of the secondary standard monitoring objectives is likely that the detection limit of 1 ppbv would be acceptable. Maximum interference shall be less than ±5 ppbv SO_2 equivalent, and 12- and 24-hour zero drift less than ±5 ppbv SO_2 equivalent. Presumably these metrics are also acceptable but in the absence of guidance on the anticipated mixing ratios that would be relevant, a recommendation is premature.

Charge Question 4: What are the panel's views on using existing NOy methods that are deployed, for example, in NCore as the measurement approach for NOy for the purpose of providing annual average values as an indicator for the NOx/SOx standard? What are the panel's views on EPA's assessment that additional study is needed before establishing an FRM based on the existing NOy methods? That is, are the methods already adequately demonstrated as a reference method to determine compliance with a NAAQS? What are the panel's views on the research plan for establishing existing NOy methods as an FRM? [Note suggested improvement to the plan would be appreciated, particularly ones that would help complete the study on time.]

I have no preliminary comments on this charge question.

Charge Question 5: What are the panel's views on using the emerging AMoN ammonia monitoring network that uses passive sampling technology as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?

Some information is available on the data quality from the AMoN ammonia monitoring network.[1] Measurements were conducted using Radiello® passive samplers. Triplicate samplers were used to determine precision and URG denuders were used to determine relative accuracy. These data should be packaged and disseminated to provide insights into the measurement data quality.

[1] "NAPD's New Network: AMoN The Passive Ammonia Monitoring Network", M. Rury, EPA/CAMD.

Charge Question 6: What are the panel's views on co-locating ammonia measurements at each location where the indictors are measured?

This would have added value and, presuming the passive sampling approach is deemed to have acceptable data quality, it would require a low level of effort for field operations.

Charge Question 7: What are the Panel's views on using the CASTNET filter pack (FP) to measure ammonium ion as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?

See comments for sulfate above, #1.

Charge Question 8: What are the panel's views on establishing a suite of NO_y species measurements at 2- 5 locations in different atmospheric and ecological regions for the purpose of evaluating air quality model and NO_y instrument behavior?

I have no preliminary comments on this charge question.

Charge Question 9: What are the panel's views on utilizing the existing CASTNET and rural NCore networks as a starting infrastructure for the purpose of supporting the NO_x / SO_x standard?

Both CASTNET and the rural NCore sites provide an excellent opportunity to leverage existing infrastructure and should be exploited when practicable.

Charge Question 10: What are the panel's views on using CASTNET filter pack (FP) to measure total nitrate (particulate nitrate plus nitric acid) as the measurement approach for the purpose of providing annual average values to support the NO_x / SO_x standard in diagnosing NO_y instrument behavior and assist in delineating the relative fractions of contributing oxidized nitrogen species to total ambient oxidized nitrogen.

See comments for sulfate above, #1.

Charge Question 11: What are the panel's view of the broader consideration of using CASTNET, complemented by rural NCore, to serve as a framework for the nation's rural monitoring of important gases and aerosols in support of secondary standards and evaluating the behavior of regional air quality models?

Based on the provided background information, the existing CASTNET and rural NCore network infrastructure provide a solid framework in support of the secondary standards and also to support the modeling effort. The existing sites are generally well-aligned with the identified eco-systems with perhaps the exception of the northwest United States. It would be very helpful to get input from the modelers about desirable monitoring locations outside of the identified eco-sensitive regions. For example, there are large gaps in areas such as the Central Plains; would this be an important area for monitoring to support model evaluation?

Comments from Dr. Yousheng Zeng

GENERAL COMMENTS

1. The proposed NO_x / SO_x secondary NAAQS takes a form (Aquatic Acidification Index, or AAI) that will require many parameters to be put in an equation to determine attainment with the standard. Some of these parameters will be determined by ecosystem's characteristics on a region-by-region basis among the 84 ecoregions covering the continental U.S.; some of the input parameters will come from the CMAQ model; and some will come from monitoring instruments. As of now, all NAAQS (primary or secondary) are based on direct measurements of pollutant levels in ambient air. Other than averaging or statistic schemes used to construct a proper form of the standards, no other modeled parameters are introduced as important components of the standards. The proposed NO_x / SO_x secondary standard is a dramatic departure from this long-established practice. This approach may be needed due to the nature of the ecosystems that this standard is set to protect. However, we need to keep in mind that unlike other NAAQS, there are a lot of relatively judgment-based parameters and model-based parameters being introduced into this standard. Through our knowledge in working with various air quality models, we understand that there are significant levels of uncertainties associated with these complex models. For example, Table F-2 in Appendix F to the final Policy Assessment (PA) shows that the bias ranges from -17% to 47%. It may not be productive and cost-effective if we pursue the same level of perfection as we do with monitoring methods for traditional NAAQS where compliance is solely determined by measurements. Incremental gain in monitoring accuracy may become insignificant compared to the uncertainties introduced by judgment-based and model-based parameters.

2. The indicators measured for the NO_x / SO_x secondary standard are NO_y, SO_2, and p- SO_4; and they are measured as ambient concentrations, not atmospheric deposition. The fundamental concern of this secondary standard is acid deposition, which include wet and dry depositions. In this form of standard, the wet deposition is accounted for through model-based components in the AAI equation. My understanding of EPA's approach is to apply one set of these judgment-based and model-based parameters to each of the 84 ecoregions. Each ecoregion could be large enough to cover areas that have substantially different annual precipitation. When one part of an ecoregion experiences significantly more precipitation than another part of the same ecoregion, the indicators to be monitored (NO_y, SO_2, and p- SO_4) will be significantly lower when the precipitation scrubs out these species from atmosphere. However, everything else in the AAI equation will remain the same. The area with more precipitation will have lower ambient concentrations of NO_y, SO_2, and p- SO_4 and a better AAI, but the more acid deposition may have occurred and the impact to the ecosystem is not necessarily lower as indicated by AAI. It seems to me that wet deposition should be directly measured.

3. I like the idea of using the FP (or with some modification) to measure everything needed in the AAI equation. Without modification, the FP can measure SO_2 and p- SO_4 well. It cannot measure NO_y. However, it can measure p-NO3 and HNO_3, i.e., t-NO3. Conceptually, t-NO3 can be used as a surrogate for NO_y and F3 in the AAI equation can be adjusted from a NO_y referenced parameter to a t-NO3 referenced parameter.

   Alternatively, the FP can be modified by adding a denuder to measure NO_x. Then the sum of NO_x, p-NO_3, and HNO_3 can be used to represent NO_y in the AAI equation.

   Considering uncertainties introduced by modeling aspect of the AAI, using one of these surrogates for NO_y seems very reasonable. It will make the monitoring for secondary standard significantly easier and more cost-effective.

4. Reduced nitrogen (NH_3 and NH_4) seems significant in the AAI equation. Measurement methods exist for these species. NH_4 is already measured by CASTNET FP. What is the rationale to have some parameters (e.g., NO_y, SO_2, and p- SO_4) measured and other (e.g., NH_4, NH_3) modeled? Even if a measurement for NH_4 is less than ideal, it may still be better to directly measure it than to rely on a fixed modeled value because it should better account for spatial variability and provide some consistency across the parameters used in this standard. The argument that NHx is not a criteria pollutant and therefore should not be explicitly expressed in the AAI equation is not very convincing because NHx is still incorporated in the AAI equation through F2 and there are some species in NO_y and SO_x that are not criteria pollutants.

RESPONSES TO SPECIFIC CHARGE QUESTIONS

Charge Question 1 - Use of CASTNET Filter Pack to Measure Particulate Sulfate

Response: Using CASTNET FP to measure p- SO_4 for the purpose of the NO_x / SO_x secondary NAAQS makes sense. It is a well established method for similar application, i.e., measuring acid deposition in CASTNET. It is relatively simple and cost-effective. A disadvantage of this method is that it measures weekly average value and lacks the time resolution for studying daily or hourly changes, which can be very valuable information for model evaluation and other purposes. However, for monitoring compliance with this annual standard, this method is adequate. Even after some hourly measurement instruments (e.g., MARGA) is well developed, the CASTNET FP is expected to be a lower cost method. For the same budget, the disadvantage of poor temporal resolution can be traded off for better area coverage, i.e., having more monitoring locations. Better temporally resolved instruments can be deployed at a few selected sites (or on rotation with a mobile/transportable platform) for better understanding of temporal variability.

From regulatory viewpoint, determination of attainment with NAAQS, either primary or secondary, should be based on monitoring results generated by FRM or FEM. It seems that if the CASTNET FP method will be used for determination of attainment with the NO_x / SO_x secondary NAAQS, it will be more defendable to give this method a FRM or FEM status. For aforementioned reasons, I would support EPA's effort to develop the FRM specifically for the NO_x / SO_x secondary NAAQS based on the CASTNET FP method.

Charge Question 2 - Use of CASTNET Filter Pack to Measure Sulfur Dioxide Gas

Responses: The manual FRM for SO_2 has been established for a long time, but not commonly used now. Continuous SO_2 FRM monitoring instruments are commercially available from various vendors. These instruments are well established and widely deployed. From the viewpoint of the technology, there would be no need to develop another FRM based on a less sophisticated method. Designation of area attainment with NAAQS, either primary or secondary, is always based on FRM or FEM. If a designation is made based on non-FRM or non-FEM, the decision may be contested. To avoid this situation, a continuous SO_2 FRM or FEM monitor would need to be deployed. However, the most CASTNET sites do not have a continuous SO_2 FRM/FEM analyzer. For the purpose of determining compliance with the NO_x / SO_x secondary standard, a continuous SO_2 FRM/FEM analyzer is not necessary. If EPA has sufficient data (or conduct additional study) to show that weekly averaged results generated by a continuous SO_2 FEM analyzer are consistent with the results from CASTNET FP, it would be desirable to establish the CASTNET FP method as the FRM specifically for the NO_x / SO_x secondary NAAQS (and not applicable to the primary NAAQS). Has EPA evaluated the accuracy/consistency between the SO_2 measured by the CASTNET FP and the SO_2 measured by a continuous SO_2 FRM analyzer averaged over a week?

Most sites for the NO_x / SO_x secondary standard monitoring network are expected to be in rural areas where SO_2 concentrations could be very low. The concentrations could approach or even be below the method detection limit of current continuous SO_2 FRM analyzers. If that is the case, making the FP method for SO_2 a FRM would be very important.

If EPA anticipates that a large number of monitoring stations for the NO_x / SO_x secondary standards will be standalone and not be co-located with stations in other networks, it will be better to use the FP to measure SO_2. This will be more cost-effective and the measurement averaging time will be synced with that of p- SO_4.

Charge Question 3 - Use of Current Primary FRM (High Time Resolution UVF) to Measure Sulfur Dioxide Gas

Response: As mentioned in Response to Charge Question 2, the method detection limit of the current primary FRM may not be low enough to measure very low SO_2 levels on the continuous basis at some rural sites. The CASTNET FP method measures amount of SO_2 accumulated on the filter over a one week period. I would prefer the CASTNET FP method being FRM for NO_x / SO_x secondary standard monitoring. EPA is conducting a comparative study of the FP method and the current FRM, If the study shows that the results of FP are consistent with the results of primary FRM, The UVF based, continuous FRM can be designated as FEM for the secondary standard in addition to FRM for the primary standard, provided that SO_2 concentrations are well above the method detection limit of the continuous method. All secondary standard monitoring sites should be equipped with FP. A few selected sites could be equipped with a continuous SO_2 FRM analyzer (or on rotation with a mobile/transportable platform) for better understanding of temporal variability.

Charge Question 4 - Use of Existing NOy Methods

Response: With regard to NO_y method, see my General Comment 3.
Comments with regard to EPA's research plan: The plan includes an effort to evaluate the FP SO_2 method for potential FRM/FEM. I highly support this effort and strongly encourage EPA to elevate the level of importance of this element in the research plan. I am concerned by EPA's notion that there is already FRM and FEM for SO_2 and therefore there is no need to establish additional SO_2 FRM or FEM for the NO_x / SO_x secondary standard. I do think that having a FP based SO_2 FRM or FEM is very important for the reasons discussed in my Responses to Charge Questions 2 and 3.

The idea of using t-NO3 measured by FP as surrogate for NO_y is very attractive. If this approach is demonstrated to be acceptable in the context of NO_x / SO_x secondary NAAQS, the monitoring network for NO_x / SO_x secondary NAAQS could be made of nothing but CASTNET FP type monitors to collect all parameters (SO_2, p- SO_4, and NO_y) needed to determine compliance with the secondary standard. The FP based monitors can form the backbone of the monitoring network and the network can be supplemented by a higher tier, more sophisticated SO_2 and NO_y analyzers deployed at a few selected sites or on a rotation basis. Even if t-NO3 is not an adequate surrogate for NO_y, the established NO_x monitors could be used so that the combined results of NO_x from NO_x analyzer and t-NO3 from FP can cover the majority (probably >90%) of NO_y. Also see my General Comment 3.

A FRM/FEM is needed for NO_y for reasons discussed in my Responses to Charge Questions 1 and 2.

Charge Question 5 - Use of the Emerging AMoN Ammonia Monitoring Network

Response: I am not familiar with AMoN. If the sampling methods can provide the time resolution suitable for model evaluation, they should be used for this kind of study along with measurements of other species (e.g., NO_y) in the same time resolution.

Charge Question 6 - Co-Locating Ammonia Measurements

Response: It is not clear to me concerning the purpose of co-locating NH_3 with measurements of other indicators. If the purpose is for model evaluation, the time resolution should be finer than weekly and it should be co-located with other measurements with finer time resolution (see my response to Charge Question 5). If the purpose is for compliance, ammonia measurement value is not used in the AAI equation. This may make sense if EPA considers including NHx measurement in the AAI equation (see my General Comment 4).

Charge Question 7 - Use of CASTNET Filter Pack to Measure Ammonium Ion

Response: It should be an area for EPA to explore. My initial thought on this is the sampling time. If the purpose is to study the model behavior, will the time resolution of the weekly data sufficient? I am not familiar with the FP method for ammonium. Is there a concern about any portion of ammonium being lost due to vapor pressure of some ammonium salt? Also, I am not sure if the FP method can provide information on relationship between ammonium and ammonia.

Charge Question 8 - Establishment of a Suite of NOy Species Measurements

Response: I would support this approach. However, the measurement should not be limited to species within NO_y. At least NH_3 and NH_4 should be included for model evaluation. It seems that instruments such as MARGA will be suitable to this type of sites. For this purpose, even if the absolute accuracy of the measurements is not high, relative relationship and behavior will be useful.

Charge Question 9 - Use of CASTNET Filter Pack and Rural NCore Networks as a Starting Infrastructure

Response: I think the CASTNET and rural NCore network will be a good starting point for the NO_x / SO_x secondary NAAQS monitoring network. If EPA can determine that the CASTNET FP method can adequately measure SO_2, p- SO_4, and NO_y, directly (SO_2 and p- SO_4) or through a surrogate (t-NO3 as a surrogate for NO_y), balancing the uncertainties that exist in other components of the AAI equation and the requirements for measurement accuracy, this approach

will facilitate implementation of the new secondary standard in a shorter timeframe and with lower cost.
A question I have is – are there any sensitive ecoregions that are not adequately represented by the CASTNET network?

Charge Question 10 - Use of CASTNET Filter Pack to Measure Total Nitrate

Response: If EPA decide to use NO_y instrument, EPA should use FP along with NO_y instruments for the purposes stated in this question. According to the current Research Plan, it seems that EPA will use existing data for similar analysis but not actually perform side-by-side measurements between FP and NO_y instrument. It would be very beneficial to include FP in this well structured lab and ambient study to evaluate the relationship between the two measurements (and other measurements planned in the study). Through this study, EPA may be able to evaluate feasibility of using t-NO3 as surrogate for NO_y (see my General Comment 3 and Responses to Charge Question 4).

Charge Question 11 - Broad Consideration of Using CASTNET, Complemented by Rural NCore, As A Framework for National Rural Monitoring

Response: With regard to evaluating the behavior of regional air quality models, the biggest concern is the time resolution. The CASTNET FP method measures these species on weekly average basis. This will not have time resolution fine enough to evaluate model behavior.

Compilation of Comments from Individual Members of the CASAC NO_x And SO_x Secondary NAAQS Review Panel

Comments from Dr. Andrzej Bytnerowicz

Reponses (only to the questions where I have adequate knowledge and experience)

Charge Question 5: What are the panel's views on using the emerging AMoN ammonia monitoring network that uses passive sampling technology as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?

Answer: This is a good approach that can produce reliable results of the time-integrated (week to a month) concentrations of ammonia. There are several types of the commercially available passive samplers for ammonia that can produce reliable results. AMoN monitoring network is needed because of an absence of reliable, practical and cost-effective electronic monitors and uncertainties of the CMAQ predictions of the NHx ambient concentrations.

Charge Question 6: What are the panel's views on co-locating ammonia measurements at each location where the indicators are measured?

Answer: This is a good idea that should help in understanding spatial and temporal patterns of ammonia distribution based on the experimental data. Collocation of ammonia passive samplers with the CASTNET filter packs could also help in understanding what proportion of ammonium nitrate collected on Teflon filter has volatilized. I suggest adding also passive samplers for nitric acid that have been successfully used in the various parts of the US and Canada. Collocating ammonia and nitric acid passive samplers with the CASTNET filter packs could be useful in evaluation of the mentioned above problems related to the ammonium nitrate volatilization.

Charge Question 7: What are the Panel's views on using the CASTNET filter pack (FP) to measure ammonium ion as a tool for evaluating air quality model behavior with respect to characterizing ambient air patterns of ammonia?

Answer: That would only be useful if another filter (citric acid or phosphoric acid coated) is added to the filter pack to collect ammonia resulting from the ammonium nitrate volatilization. At the same time ammonia should also be measured with the collocated passive samplers.

Charge Question 8: What are the panel's views on establishing a suite of NOy species measurements at 2 -5 locations in different atmospheric and ecological regions for the purpose of evaluating air quality model and NOy instrument behavior?

Answer: That should be done with the chemiluminescence instruments for total NO_y. In addition, passive samplers for NO_x, NO_2, and HNO_3 should also be deployed.

Charge Question 9: What are the panel's views on utilizing the existing CASTNET and rural NCore networks as a starting infrastructure for the purpose of supporting the NOx/SOx standard?

Answer: This is a very good idea. If I am correct, the proposed network would probably use the Radiello samplers. There are also other samplers of a similar reliability (such as Alpha or Ogawa). It would be good to coordinate these efforts with the ongoing monitoring of ammonia with the Ogawa passive samplers in the western US, especially in southern California and the Sierra Nevada (especially the Lake Tahoe Basin).

Charge Question 10: What are the panel's views on using CASTNET filter pack (FP) to measure total nitrate (particulate nitrate plus nitric acid) as the measurement approach for the purpose of providing annual average values to support the NOx/SOx standard in diagnosing NOy instrument behavior and assist in delineating the relative fractions of contributing oxidized nitrogen species to total ambient oxidized nitrogen.

Answer: The filter pack is capable of measuring total nitrate by collecting particulate nitrate on the Teflon filter and nitric acid on the nylon filter. Major problem of this method is that the proportion of the measured particulate vs. gaseous fractions is unreliable. Due to the ammonium nitrate volatilization to nitric acid and ammonia it is unknown how much of the nitrate deposited on the Teflon filter has remained in particulate form, and how much has been decomposed and added to nitric acid collected on the nylon filter.

Due to the above mentioned ammonium nitrate volatilization issues, the CASTNET filter pack as presently used would be a very poor tool for supporting the NO_y measurements conducted with the electronic monitors.

Charge Question 11: What are the panel's view of the broader consideration of using CASTNET, complemented by rural NCore, to serve as a framework for the nation's rural monitoring of important gases and aerosols in support of secondary standards and evaluating the behavior of regional air quality models?

Answer: This is a very good idea, especially if additional measurements with passive samplers and some other techniques (e.g., remote sensing) are also considered. In addition the meteorological data collected at the CASTNET sites (especially temperature) would improve quality of data derived from the passive samplers (correction for diffusion rates). The Forest Service will soon start monitoring of air quality (ozone and reactive gaseous N species) on a national network of the Experimental Forests and Ranges. That will be done in collaboration with the CLAD activities under the umbrella of NADP (collaboration between FS, NPS, EPA, USGS and academia).

Comments from Mr. Rich Poirot

Charge Question 1: What are the Panel's views on using the CASTNET filter pack (FP) to measure particulate sulfate for the purpose of providing annual average values as an indicator fort the NOx/SOx standard? Given EPA plans primarily to document the capability of the CASTNET FP and develop the FRM for particulate sulfate based on the existing information and procedures, what are the Panel's views of this approach for setting the FRM?

The proposed use of the CASTNET Filter Pack (CFP) as an FRM for sampling particulate sulfate for this secondary NAAQS application seems adequate. The method has been relatively well-characterized and evaluated, and has a documented long-term track record of successful use in a field network designed to assess spatial patterns and long-term temporal trends. Because the CASTNET network plays an important role in tracking CAA-related air quality changes over space and time (regardless of new standards), I also think the program as a whole will benefit from the more detailed scrutiny that would result from FRM development, and subsequent use in a compliance application. For example it has been observed that the error associated with long-term CASTNET (and other) sulfate trends may be larger (about 1%/yr) than has previously been estimated (White *et al*., 2005), and efforts to further reduce that uncertainty would be welcome.

A major advantage of specifying the CFP for sulfate is also to maintain the possibility that the CFP might conceivably be used to supply all the measurements required to implement this NAAQS, assuming that an FEM could be specified for CFP SO_2 and that "total nitrate" (and an associated deposition transfer ratio) could be used as a surrogate for NO_y in the AAI equation. The resulting network might employ a mix of weekly filter-based and continuous methods, and address the multiple objectives of compliance determination, model evaluation /improvement, and more complete atmospheric characterization – without the need to do everything everywhere

The time resolution of the resulting CFP weekly data is adequate for (partially) determining compliance with a NAAQS with a 3 to 5-year averaging time, and sampling all the time will reduce the inter-annual variability introduced by intermittent (1 in 3 day) daily sampling in programs like IMPROVE and CSN (or avoid the excessive costs of operating such filter-based networks daily). Weekly time resolution is minimally useful for model evaluation and refinement, and for that objective, it would be highly desirable to consider deployment of continuous sulfate analyzers at a few sites where continuous SO_2 is being measured. See for example Drewnick *et al.* (2003). While continuous sulfate analyzers are typically operated with size selective inlets, they don't necessarily need to be run that way. Although, for model evaluation purposes (if not for NAAQS determination), a 2.5 micron inlet might actually be desirable for continuous sulfate. Specifically, I don't expect CMAQ to have much skill in calculating coarse sulfate concentrations, and adding some coarse sulfate into the measurement, without knowing how much or in what size bin is not likely to help improve the model.

For similar reasons, I don't completely agree with staff arguments that the open-faced CFP sampler is critically necessary to include capture of coarse sulfate particles. I think this is harmless but probably not very helpful (and is in any event not very important- a few percent of the problem at most). This is not a purely measurement-based NAAQS, nor one focused directly on measured deposition, but rather one that relies on a combination of air concentration measurements and model results. The estimated total S deposition (aggregated over multiple years and spatially large ecoregions) is the product of the measured SO_x indicator and the CMAQ T SO_x deposition transfer ratio. The best indicator is not the one which includes (as open-faced sulfate might) a bit more of the species which dry deposit most efficiently. The best indicator is the one with the best and most stable correlations over both space and time with total S deposition. I doubt that CMAQ has much skill in predicting coarse particle sulfate concentrations or deposition, and I further question the ability of an (affordable) monitoring network to adequately capture the spatial variability of coarse particle sulfate concentrations. Further, the open faced collector provides no information on what fraction of the resulting sulfate is in the larger, more rapidly dry-depositing size range, or what the sizes of those larger particles are. The SO_x indicator is proposed to be the simple, linear sum of atmospheric S from (rapidly dry depositing) SO_2 and (much more slowly depositing) particulate SO_4 (with no attempt to weight this sum by the relative deposition velocities, for example). I don't believe that it can be demonstrated that a SO_x indicator which includes an unknown amount of coarse sulfate, combined with a CMAQ T SO_x deposition transfer ratio which also includes coarse sulfate (for which the model performs poorly) can be shown to be a superior indicator over space and time than a combination of measure and model ratio which excludes coarse particles.

During the 2003/ 2004 IMPROVE coarse particle characterization study (Malm et al., 2007), there was more coarse particle nitrate than sulfate at all 9 of the rural, nationally distributed IMPROVE sites included in that study. Crustal material, which tends to be alkaline, accounted for more than half the coarse mass at all sites, and so it seems highly unlikely that the relatively small amounts of coarse N and S contribute an "acidifying" effect that is not more than countered by associated deposition of base cations (not considered in the AAI equation). It also seems likely that much of the coarse sulfate and nitrate may be associated with mineral cations (Ca^{++}, Mg^{++}, K^+, Na^+, etc.), and this coarse mineral nitrate (which exceeds coarse sulfate) may not be efficiently captured by, or fully converted by the proposed NO_y samplers. Conceivably, there could be a bit of positive sampling artifact if acid gases react with alkaline coarse crustal material on the open faced filters, although this would be quite small and minimized or offset if it's the sum of PM and acid gas compounds (from the same CFP) that's used as the indicator.

As indicated above, I generally support the specification of the CFP as p-SO_4 FRM for this standard, and think it would be highly desirable to add a few continuous sulfate analyzers at sites with continuous SO_2 for model evaluation/improvement purposes. I think it would also be useful if the proposed HEASD Research Plan for FRMs for NO_y and p-SO_4 were accompanied by a parallel effort to look more closely at CMAQ concentrations, deposition and species ratios over space and time. Can it be demonstrated that inclusion or exclusion of coarse sulfate improves

the overall measure+model total S deposition estimate? Might there be a comparable measure + model combination using SO_2 and fine sulfate only. Does a linear sum of gas and particle S (or N) species make the best indicator over space and time, or might a weighted sum work better? What is the spatial variability of the modeled species concentrations, depositions and transfer ratios within the identified ecoregions? How would measure+model N deposition estimates compare if based on CFP total nitrate rather than NO_y, etc.?

Charge Question 10: What are the panel's views on using CASTNET filter pack (FP) to measure total nitrate (particulate nitrate plus nitric acid) as the measurement approach for the purpose of providing annual average values to support the NOx/SOx standard in diagnosing NOy instrument behavior and assist in delineating the relative fractions of contributing oxidized nitrogen species to total ambient oxidized nitrogen.

Based on the (revised) Figure 2-32 in the Final 2/11 Policy Assessment Document (and monitoring summary) as well as Figure 4-21 from the 9/10 Draft PAD, it appears that nitric acid would be as good an indicator (or better) than NO_y for predicting total oxidized N deposition (if combined with a matched CMAQ deposition transfer function). I assume the total nitrate (sum of particulate nitrate and nitric acid) available from CASTNET Filter Pack (CFP) samples would also make for an adequate indicator of total N deposition. This could easily be evaluated by exploring the stability of CMAQ ratios of total nitrate to total oxidized N deposition over space and time (with decreased NO_x emissions). Assuming this indicator is suitable, and that SO_2 from the CASTNET filter pack was also suitable (combined with CFP SO_4) as a SO_x indicator, all measurements needed to implement the standard could be taken by the CFP method.

While the weekly time resolution of CFP data would be adequate to determine compliance with a standard averaged over 3 to 5 years, such data would be much less useful for purposes of model evaluation and refinement and overall atmospheric characterization than that which could be provided by the use of continuous SO_2, SO_4 NO_y or speciated NO_y measurements. Given current budgetary constraints, a network composed of relatively inexpensive CFP samplers at many sites, complemented by continuous samplers for the various relevant species at a subset of sites might be a reasonable approach.

It was interesting to note in the HEASD Methods research plan that while HEASD "<u>will</u>" conduct a thorough evaluation of the NO_y method, and "<u>will</u>" propose and finalize FRM specifications for NO_y, HEASD only "<u>may</u> consider, as resources allow" an additional FRM or FEM using the CFP t-NO_3 method "due to the <u>expected prohibitive cost</u> associated with equipping a site with NO_y monitors". Hmmm… I think it should be a somewhat higher priority to evaluate the suitability of the CFP t-NO_3 method as potential indicator (combined with an equivalent CMAQ deposition transfer function). The Methods Research Plan should also be complemented with a much more detailed evaluation of the CMAQ model results for all the various N and S species concentration, deposition and transfer ratios. For example, from CMAQ

alone, what would be the differences over space and time in estimated total oxidized N deposition if NO_y or tNO_3 were used as indicator (quite small I suspect)? Perhaps this would allow a mix of methods with different measured indicators but comparable measure+model deposition estimates. The suitability of the CFP t-NO_3 (and SO_x) method(s) could also be (approximately) assessed using historical CASTNET concentration and dry deposition + NADP wet deposition data. See for example Butler et al. (2011), etc.

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