# AMBIENT AIR MONITORING FOR A NEW SECONDARY NAAQS FOR OXIDES OF NITROGEN AND SULFUR

The NOx/SOx welfare panel has advised EPA that ambient air measurements of nitrogen and sulfur species support implementation of this proposed NAAQS secondary standard and improve the information basis for subsequent reviews. These uses extend beyond the basic need to measure the proposed NAAQS indicators, $NO_Y$, $SO_2$ and $SO_4$, in approximate priority order:

- Direct NAAQS comparisons.
- Reduced nitrogen, $NH_3$ and $NH_4$, to evaluate CMAQ and other air quality models ability to characterize $NH_X$ deposition, a component of the AAPI expression.
- Model and process improvement - In combination with NAAQS indicators and NHx, additional speciated $NO_Y$ components including $HNO_3$, PAN, $NO_2$, and NO to continually assess air quality model behavior and associated deposition processes.
- Subsequent NAAQS reviews of the secondary $NO_X/SO_X$ standard as well as related primary and secondary standards reviews (ozone, $NO_2$, $SO_2$ and PM).
- Accountability – Assessing the effectiveness of implemented programs addressing emission strategies to meet attainment of the proposed NAAQS using all noted measurements.

## 8.1 What Are The Appropriate Ambient Air Indicators To Consider In Developing The Standards?

The recommendation of $NO_Y$, $SO_2$ and $SO_4$ as the ambient air indicators for the proposed $NO_X/SO_X$ standard was introduced in the first draft of the PAD and endorsed by CASAC (CASAC, 2010). Essentially, $NO_Y$, which is an aggregate of all reactive oxidized nitrogen compounds and the two sulfur species represent the oxidized ambient air species of relevance to the criteria pollutants $NO_X$ and $SO_X$ with potential to adversely affect acid-base balance in aquatic systems. Contributions of reduced nitrogen, which would not be part of the indicator for the standard under the approach suggested in this PAD, are provided by CMAQ.

1

*Why not use each individual species as indicators?*

One could consider using all $NO_Y$ species as NAAQS indicators, requiring, for example, measurements of the dominant species: $HNO_3$, particulate nitrate, $NO_2$, NO, and PAN. Conceptually, each species would be paired with a species - specific deposition velocity in the AAI expression to transfer individual deposition values to ambient values. The attraction of using individual species would be the reliance on actual deposition velocities that have more physical meaning in comparison to model constructed transference ratios which aggregate dry and wet deposition and all nitrogen species. The transference ratio approach does retain the necessary conservation of mass which underlies virtually all parameterization schemes, but loses some degree of physical relevance due to use of modeled outputs – an admittedly unique construct. The major drawback of using individual species as NAAQS indicators is the lack of routinely available measurement techniques and an associated resource burden even if adequate techniques were available. Currently, technology for measuring true $NO_2$, $HNO_3$, and PAN generally is not available for routine network applications. In addition to this practical consideration, there is another important reason for using the aggregated transference ratios. Because the standard, and the explicit Clean Air Act authority, is based on ambient air there must be an effective link connecting deposition and concentrations of the criteria pollutants in the ambient air. The use of individual species conceptually allows for a more physically meaningful approach to characterize and calculate deposition. However, the transference ratios also enable incorporation of the contributions of wet precipitation in the ambient air indicators. There is no practical alternative that allows for the disentangling of wet deposition as a function of ambient air concentrations as that relationship is best addressed through the coupling of numerous meteorological and chemical processes imbedded in the air quality modeling platform. One could consider wet precipitation as a separate parameter and isolate dry precipitation in the AAI equation. But doing so would lose the important connection between wet precipitation of nitrogen and the same emission sources responsible for dry deposition.

Another way of addressing the relative benefit of using part of the NOy mix relative to total NOy in regard to deposition is to probe the dynamic response of changes in oxidized nitrogen deposition to changes in ambient concentrations NOy and nitric acid. Dynamic

1  response refers to sensitivity of the ambient to deposition response with respect to changes in

2  NOx emissions, which is relevant to air quality management as ambient indicators are used to

3  assess if an area meets or exceeds a target value in current and future time frames.   While such a

4  response to emission changes may be linear or non-linear, the details of which are encoded in

5  chemical transport air quality models like CMAQ, typically there is a directional relationship

6  between the change in the precursor emissions and the target species of interest.   By extension,

7  one would expect that a significant change in emissions of NOx would lead to a change both in

8  the ambient and deposition fields of NOy species, recognizing that NOy species all evolve from

9  NOx emissions, which is dominated by nitrogen oxide, NO.  We can apply this reasoning to the

10  consideration of using HNO3 as a more narrowly defined indicator, relative to NOy.  A 2005

11  base case and projected 2030 CMAQ simulation, with roughly 50% NOx and SOx reductions,

12  respectively, are used to illustrate the relationship of HNO3 and NOy concentration changes to

13  changes in NOy deposition (wet and dry) which address the question:   Does the indicator

14  respond in a manner directionally similar to deposition over periods of significant emissions

15  reductions?  Based on this paired set of current and future projection scenarios, ambient NOy

16  more closely captures the change in NOy deposition, compared to using ambient HNO3 as an

17  indicator (figure 8-7 ).

18

19

20       Finally, one might advocate for direct measurements of dry deposition of individual $NO_Y$

21  species.  Again, technologies simply are not ready for consideration in routine network

22  applications.  And, it is arguably practical to model dry deposition even if direct dry deposition

23  measurement technologies were available.  One reason for this is that there is significant spatial

24  heterogeneity in the factors (vegetation and surface type, micrometeorology) that define

25  deposition velocity.  Consequently, direct dry deposition measurements would have limited

26  spatial representativeness in comparison to ambient air observations.   The model conceptually

27  accounts for the spatial variance, at the level of horizontal grid cell resolution, of the factors

28  defining deposition velocity on a species by species basis.  However, one also could reason that a

29  well placed direct measurement of dry deposition is more realistic than a modeled result that

30  relies on numerous assumptions.  The development of technologies to measure direct dry

31  deposition will benefit the diagnosis and improvement of process formulations in models.

1

Consideration has been given to change the atmospheric indicator from $NO_Y$ to total nitrate (the sum of nitric acid and particulate nitrate).   The rationale for that approach is that a larger fraction of the deposited $NO_Y$ is accounted for by total nitrate, which currently is measured in CASTNET with high confidence.  One can reason adequately that nitrate may correlate well with total oxidized nitrogen deposition relative to $NO_Y$, given the inherent noise associated with variable contributions of low deposition velocity species of ambient level significance (e.g., $NO_2$).  The disadvantages of using total nitrate as an indicator are that significant ambient mass with the potential for deposition is not captured, and $NO_Y$ is a preferred measurement for model evaluation and accountability purposes.  Accountability refers to assessing if emissions reductions have the intended consequences on ambient air and deposition levels in the context of, "Aare our emissions reductions strategies working as planned?" All three of these concerns relate to the benefit of closing mass balances in whatever environmental medium is being characterized.   In addition, the use of nitrate alone would create an increased distancing from the listed criteria pollutant oxides of nitrogen as $NO_Y$ does include NO and $NO_2$.

**8.2     Reactive Oxidized Nitrogen and Sulfur Species.**

*$NO_Y$ species.*  Air quality models and deposition models that use direct observations calculate 'deposition on a species by species basis to account for differences in deposition velocities.  Consequently,  the relative fractional contributions of individual $NO_Y$ or $SO_X$ species to deposition or concentration is influenced by the differences in species deposition velocities.  For example, nitric acid with a high deposition velocity would exhibit a larger relative contribution to overall deposition compared to ambient concentrations in a particular area (Figure 8-1).   The dominant ambient air $NO_Y$ species are NO, $NO_2$, $HNO_3$, $P-NO_3$ and PAN.  Near source urban environments typically have a relatively higher fraction of NOx compared to the products of $NO_X$ reactions, nitrates and PAN, which are relatively more dominant in rural locations (Figures 8-2 – 8-5).

The differences in the relative patterns between ambient air and deposition on a species by species basis illustrate a number of challenges and considerations in developing a monitoring

1    strategy.  It is clear in the Adirondacks and Shenandoah areas that nitric acid is the most

2    dominant contributing species from a deposition perspective (Figure 8-1), with significant

3    contributions from particulate nitrate, PAN and $NO_2$.  The original source of emissions (NO

4    accounts for 90-95% of all emitted $NO_X$) provides very small ($< 5\%$) contributions to ambient air

5    and virtually nothing to deposition.   The combination of nitric acid and particulate nitrate

6    consistently contribute greater than 50% of the oxidized nitrogen dry deposition load, whereas

7    PAN and $NO_2$ contribute roughly 15-25% of the deposition load.   These broad summary

8    statements speak to some of the monitoring considerations addressed earlier, particularly the case

9    for monitoring for total nitrate.  However, caution should be exercised when considering not

10   measuring a considerable fraction of the ambient $NO_Y$ burden reflected in $NO_2$ and PAN.

11   Characterization of $NO_2$ deposition is an area requiring further refinement especially considering

12   that $NO_2$ is a significant component of total oxidized nitrogen.  Zhang et al. (2005) suggest that

13   $NO_2$ contributes up to 36% of dry $NO_Y$ deposition in rural Eastern Canadian locations, and

14   suggest, based on observational evidence (Figure 8-2), that in some locations $NO_2$ deposition

15   may be similar to nitric acid contributions.

16

17         A sampling of co-located $NO_Y$ species observations in rural Eastern Canada (Figure 8-2),

18   particularly in Egbert, Ontario, illustrates the concern of the general assumption that $NO_2$ may

19   not contribute significantly to $NO_Y$ deposition in rural locations. While it may be true that in

20   general $NO_2$ is of less of concern in rural areas relative to urban areas, that does not dismiss the

21   potential for significant misrepresentation of total nitrogen budget in certain rural locations.

22

23         The results also raise the question of potential efficiencies gained from not cycling

24   between NO and $NO_Y$ analyses, which is the standard configuration in commercial NOy

25   instruments, acknowledging the limited use of NO data in rural, acid sensitive environments

26   (note that NO present in the air would still be captured in the $NO_Y$ measurement).

27

28         These examples are used to support the rationalization of using $NO_Y$ as an appropriate

29   atmospheric indicator in applying the AAPI.   However, while it may be required to measure

30   $NO_Y$ for explicit AAPI calculations to determine compliance with a NOx/SOx standard, there

31   should be additional measurements of true $NO_2$, $HNO_3$, p-$NO_3$ and PAN to allow for diagnostic

1   evaluations of both air quality models and the $NO_Y$ measurement itself.  This recommendation

2   would leverage existing CASTNET filter pack (FP) observations necessary to capture particulate

3   sulfate (discussed below) and therefore require the addition of  $NO_2$ measurements and periodic

4   sampling for PAN.

5

6   ***Sulfur Species.*** Although sulfur dioxide and particulate sulfate contribute approximately 60 and

7   40 %, respectively, to ambient SOx concentrations, sulfur dioxide is the dominant contributor to

8   $SO_X$ deposition (Figure 8-6), which is consistent with CASTNET observational studies (Sickles

9   and Shadwick, 2007).   Measurement technology issues are not as complex for SOx as they are

10  for $NO_Y$ and individual $NO_Y$ species.   Issues related to particle size fraction and averaging

11  period for SOx are discussed below.

12

13  ***Reduced Nitrogen.***

14

15      The AAPI does not include reduced nitrogen (ammonia gas and ammonium ion) as an

16  ambient air indicator.  However, reduced nitrogen deposition is an explicit AAPI component

17  which is estimated through air quality modeling.   As discussed in the Chapter 7, characterization

18  of reduced nitrogen deposition processes is an active developmental area which would benefit

19  markedly from $NH_X$ measurements in order to assess modeled predictions of ambient patterns of

20  ammonia and ammonium.   This need for monitoring ammonia in rural environments is further

21  supported by emerging evidence that ammonia acts as a regionally dispersed species based on

22  the inclusion of ammonia bi-directional flux in CMAQ simulations.  (Dennis et al., 2010).

23  Monitoring method approaches under consideration for routine application typically are limited

24  to time averaged filter and denuder technologies, including passive sampling approaches.

25

26  **8.3      What measurements would be used to characterize NOy and SOx ambient air**

27  **concentrations for the purposes of the AAPI based standard?**

28

29      Ambient NOy, $SO_2$ and particulate sulfate ($SO_4$) concentrations would be used as the

30  indicators in determining compliance with the standard. All of these indicators are measured in

31  different places within the current routine monitoring networks (section 3.2).  However, there are

1    issues requiring resolution associated with Federal Reference or Equivalency Measurement

2    (FRM/FEM) status of measurement techniques that to date have served as supplemental

3    information, which will require resolution.   A FRM for $SO_2$ exists, but not for $NO_Y$ or $SO_4$.  Only

4    recently have $NO_Y$ measurements, which historically were viewed as research venue

5    measurements, been incorporated as "routine" observations, partly as a result of the NCore

6    program.  Acquiring FRM status may require better characterization of the conversion

7    efficiencies, mass loss and clear guidance on operating and siting procedures.   Particulate sulfate

8    has been measured for several years in the IMPROVE, CASTNET and EPA CSN networks. The

9    nation has over 500 24-hour average, every third day sulfate measurements produced by the

10   $PM_{2.5}$ speciation networks (IMPROVE and EPA CSN) and nearly 80 CASTNET sites that

11   provide continuous weekly average samples of sulfate with an open inlet accommodating all

12   particle sizes.  With minor exceptions, the $PM_{2.5}$ fraction generally accounts for over 80% of the

13   ambient sulfate mass. Unfortunately, as particle size diameters increase beyond 2.5 µ,

14   gravitational settling imparts greater influence resulting in substantially enhanced deposition

15   velocities.  Consequently, the sulfate mass in size fractions greater than 2.5 µ potentially

16   provides correspondingly greater contribution to as much as 50% of dry sulfate deposition in

17   certain locations (Grantz et al., 2003).

18

19       Sample collection period is not an issue for gaseous measurements of $NO_Y$ and $SO_2$ that

20   operate continuously.  However, consideration should be given to using the CASTNET FP for

21   $SO_2$ measurements as a resource saving option, assuming the FPs will be used for particulate

22   sulfate.   However, the availability of highly time resolved data will support the continual

23   evaluation of $SO_2$ and sulfate balance in air quality modeling systems which is a critical

24   underpinning for both human and ecosystem health assessments.  Some concerns have been

25   raised about the possibility of exclusion of coarse particles from $NO_Y$ samplers operating at low

26   flow conditions as well as potential difficulties of reducing organically bound and mineralized

27   nitrate.  Insight into conversion and capture efficiency characteristics will be advanced both by

28   research catalyzed by the need to support this standard and through ongoing and future network

29   operations.

30

31   **8.4      What additional complementary measurements are recommended?**

1

2          We recommend that there be 3-4 locations nationally, in airsheds with different

3     atmospheric chemistries, that sample not only for the NAAQS indicator $NO_Y$ but for the suite of

4     major $NO_Y$ species as well; $HNO_3$, p-$NO_3$, PAN, true $NO_2$, and NO as discussed earlier. Not

5     only is this important from a modeling and process diagnosis perspective, but it is especially

6     useful in the introduction of new measurements that have a limited track record  to provide

7     insight into instrument performance.  In the case of $NO_Y$, it is even more relevant since there

8     effectively are no standards that explicitly challenge instrument accuracy given the highly

9     variable nature of $NO_Y$ species distribution and the instability associated with mixing $NO_Y$ gases.

10    This quality assurance issue is analogous to $PM_{2.5}$ where aerosol standards are not available and

11    measurement accuracy is judged against periodic challenges relative to a "gold standard"

12    instrument.  Reduced nitrogen measurements of ammonia and ammonium ion are recommended

13    at all locations with FRM/FEM instruments based on the need to support the AAPI as discussed

14    above.

15

16    **8.5      What sampling frequency would be required?**

17

18          The averaging time for the standard is likely to be an annual average, perhaps based on 3-

19    5 years of data collection to minimize the influence of interannual varaibility in meteorology,

20    especially precipitation.. Conceptually, extended sampling periods no longer than one year

21    would be adequate for the specific purposes of comparison to a standard.  However, there are

22    significant peripheral benefits relevant to improving the scientific foundation for subsequent

23    reviews and a variety of related air quality and deposition assessments to be gleaned from more

24    highly time resolved data.  In particular, the critical role of air quality models in deposition

25    assessments implies value to be derived from measurements that support model evaluation and

26    improvement.  Many of the monitoring approaches that are used throughout the nation sample

27    (or at least report out) on daily ($PM_{2.5}$ chemical speciation), weekly (CASTNET) and hourly (all

28    inorganic gases) periods.  There is a tradeoff to consider in sampling period design.  For

29    example, the weekly CASTNET collection scheme covers all time periods throughout a year, but

30    only provides weekly resolution that misses key temporal and episodic features valuable for

31    diagnosing model behavior. The every third day, 24-hour sampling scheme used in IMPROVE

1    and EPA speciation monitoring does provide more information for a specific day of interest yet

2    misses 2/3 of all sampling periods. The missing sampling period generally is not a concern when

3    aggregating upward to a longer term average value as the sample number adequately represents

4    an aggregated mean value. Additionally, there is a benefit to leveraging existing networks which

5    should be considered in sampling frequency recommendations.  A possible starting point would

6    be to assume gaseous oxidized species, $NO_Y$ and $SO_2$, are run continually all year reporting

7    values every hour, consistent with current routine network operations.  Sulfate sampling periods

8    should coincide with either the chemical speciation network schedules or with CASTNET.

9    There are advantages to coordinating with either network.  Ammonia gas and ammonium ion

10   present challenges in that they are not routinely sampled and analyzed for, and the combined

11   quantity, $NH_X$ is of interest.  Because $NH_X$ is of interest, some of the problems of volatile

12   ammonia loss from filters may be mitigated.  However, for model diagnostic purposes,

13   delineation of both species at the highest temporal resolution is preferred.

14

15   **8.6      What are the spatial scale issues associated with monitoring for compliance, and**

16   **how should these be addressed?**

17

18        The current observation network for $NO_Y$, $NH_X$ and $SO_X$ is very modest and includes a

19   monitoring network infrastructure that is largely population oriented with the exception of

20   CASTNET and IMPROVE.  While there is platform and access infrastructure support provided

21   by CASTNET, NADP and IMPROVE, those locations by themselves are not likely to provide

22   the needed spatial coverage to address acid sensitive watersheds across the United States.

23   Ambient monitoring at every watershed will not be required given the reality of  resource

24   constraints and the relative spatial homogeneity of  air concentrations that are averaged over

25   annual time periods and within 'acid sensitive" areas. The spatial monitoring requirements will

26   be associated with the determination of acid sensitive areas, which is discussed at length in

27   Chapter 5.   The number of sites per area will be addressed in rule development and general

28   guidance based on an understanding of the spatial variability of $NO_Y$, $NH_X$, sulfate and $SO_2$

29   combined with resource allocations will help inform those decisions.

30

1    Critical load models applied for the purposes of this standard would be based on annual

2    averages, which effectively serves to dampen much of the spatial variability.  Furthermore, the

3    development of an area-wide depositional load tradeoff curve implies focus on region wide

4    characterization.  Toward that end, CMAQ concentration fields will provide insight into the

5    likely spatial representativeness of monitors leading to efficient application of monitoring

6    resources.   For example, the CMAQ based spatial coefficient of variation (standard

7    deviation/mean) of oxidized nitrogen in the Adirondacks was 1.46%.  Improved dry deposition

8    estimates will result from enhancements of ambient monitoring addressing the N/S secondary

9    standards as each additional location could serves a similar role that existing CASTNET sites

10   provide in estimating dry deposition.

11

12   **8.7     What specific monitoring methods would be used?**

13

14    Federal reference and/or equivalent methods (FRM/FEM) are presently available only for

15   $SO_2$.  Particulate $SO_4$ is measured at over 500 sites nationally, and there is a general consensus

16   that methods available are reliable and provide consistent data.   $NO_Y$ measurement is in a

17   transition period from largely being viewed as a research level measurement to now  being

18   deployed as a routine measurement in EPA's national 75 site NCORE network.   The general

19   consensus on $NO_Y$ measurement is that the methodology is sound and applicable for

20   routine/regulatory use, but there does not exist a well defined understanding of the quality of

21   $NO_Y$ data.   Inorganic dry nitrate (nitric acid and particulate nitrate) is measured routinely in the

22   CASTNET network with filter packs (FP).

23

24    One of the challenges associated with specifying performance attributes for p-$SO_4$ and

25   $NO_Y$ is the lack of specific challenge standards.  For example, instruments measuring discrete

26   gases such as ozone or nitrogen oxide can be challenged by comparing an instrument's reading

27   when measuring known concentrations of gases which are readily provided for single gas

28   concentrations.  Particle standards are not available. $NO_Y$ performance typically is challenged by

29   known mixtures of $NO_2$, and occasionally with N-propyl nitrate, which only addresses part of the

30   spectrum of nitrogen species in an $NO_Y$ mix.   Consequently, instrument performance in EPA's

31   national networks for aerosol mass is quantified in terms of bias and precision relative to a co-

1    located "performance evaluation" instrument.  There is no comparable program in place for p-

2    $SO_4$ or $NO_Y$.

3

4        **p-SO$_4$.**  The routinely operating methodology for particulate sulfate (p-SO$_4$) is based on

5    an integrated (i.e., time averaged over several hours or days) sample collection on a Teflon filter

6    followed by ion chromatography (IC) detection in the laboratory.  Two major variations of this

7    approach are applied in the PM$_{2.5}$ speciation (exclusion of particles larger than 2.5 µ and 24-hour

8    collection typically every third day) and CASTNET (weekly average integrated sampling all year

9    with an open inlet to include all size fractions).  There are additional variations related to inlet

10   design and flow characteristics of PM$_{2.5}$ speciation samplers in which two designs are prevalent

11   in the networks: (IMPROVE and EPA CSN SASS samplers).  These variations are considered

12   minor as sulfate species (dominated by ammonium sulfate) typically are not subject to major

13   sampling artifacts associated with volatilization or condensation.   The difference in inlets (open

14   vs. 2.5 µ) is perceived by some as not an issue of concern as 80 - 90 % of the PM sulfate mass is

15   distributed in size fractions less than 2.5 µ.  However, the higher deposition velocities associated

16   with larger diameter particles argue for including all size fractions as discussed above.

17   Continuously operating in-situ sulfate instruments that allow for hourly, or less, data reporting

18   are available.  However, the limited deployment (less than 20 sites nationally) of these

19   instruments combined with the 2.5 µ inlet cutoff configuration preclude consideration at this

20   time.

21

22       The CASTNET FP offers three important attributes: a history of high quality data,

23   existing infrastructure and network to build on and an open inlet to capture the full range of

24   particle diameters.  EPA intends to develop FRM status for this method.   A significant

25   additional advantages of using the FP method will be the availability of important co-measured

26   species (e.g., $SO_2$, total nitrate, ammonium).   While EPA will expedite the certification process

27   for the CASTNET FP, in the future consideration should be given to other available methods to

28   more efficiently leverage network assets.  For example, the SASS sampler potentially would

29   accommodate ammonia gas and ammonium ion measurements, as well as other standard

30   chemical speciation parameters depending on the configuration of this multi channel system.

31   Continuous sulfate measurements would be extremely useful for model evaluation, especially

1     considering the availability of continuous $SO_2$ data that would be required as part of the NAAQS

2     indicators.   A performance based approach to meet equivalency requirements, given the variety

3     of sulfate measurement approaches and well vetted and accurate analytical procedures.

4

5     **$SO_2$**. Sulfur dioxide is a NAAQS pollutant and a FRM is available. See 75 FR at 35554-

6     56 and 35593-95 (June 22, 2010) (adopting a second FRM for $SO_2$).  As part of the NCore

7     network development effort, trace gas $SO_2$ analyzers capable of sub ppb resolution became

8     commercially available and are the preferred instruments for implementation in rural locations.

9     As discussed above, the near continuous data output of gaseous analyzers is desired for

10     peripheral support of model evaluation.   Nevertheless, the convenience and resource savings

11     associated with the CASTNET FP suggest that Federal Equivalency Method (FEM) status should

12     be incorporated in concert with the sulfate certification process.

13

14     **$NO_Y$.** In principle, measured $NO_Y$ is based on catalytic conversion of all oxidized

15     species to NO followed by chemiluminescence NO detection.  While there are caveats associated

16     with instrument conversion efficiency and possible inlet losses, the technique is considered

17     adequate and routinely operational.  Approximately 25 sites (out of a planned 75) in EPA's

18     NCORE network are operating $NO_Y$ instruments, and an additional 5-1 10 sites are operated in

19     SEARCH, CASTNET and other programs. $NO_Y$ measurements are nearly continuous, reporting

20     at hourly intervals providing far greater temporal information compared to filter or denuder

21     based methods.   FRM certificaton for $NO_Y$ presents more considerable challenges given the

22     limited history of routinely operating instruments.

23

24     **8.8     REFERENCES**

25

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27         Secondary National Ambient Air Quality Standard for NOx and SOx : First Draft.,
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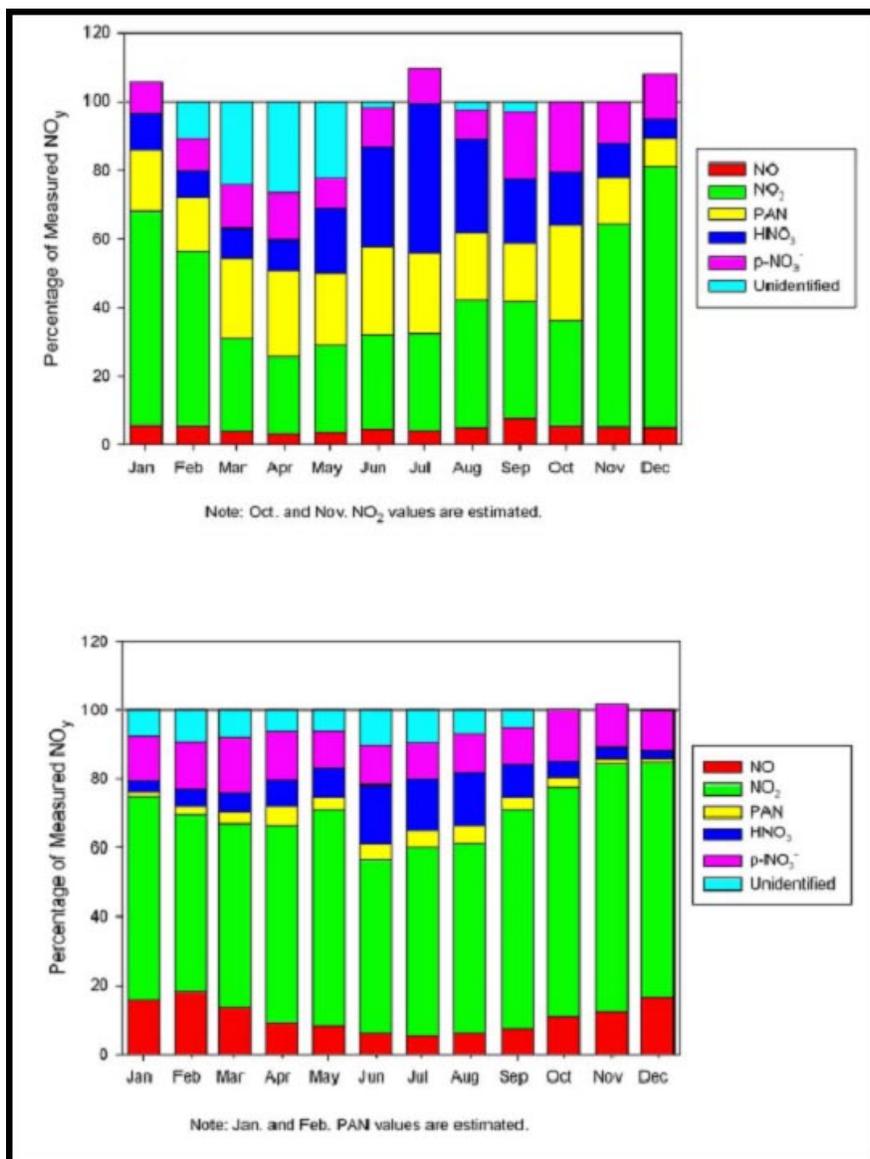34         Eastern United States: 1990- 2004, JGR, 112, D17301

1    Zhang, L., J.R. Broo, R. Vet, C. Mihele, M. Straw, J.M. O'Brien and S. Iqbal, 2005, Estimation
2          of contributions of NO2 and PAN to total atmospheric deposition of oxidized nitrogen
3          across Eastern Canada.  Atmospheric Environment 39 (2005) 7030-7043.
4
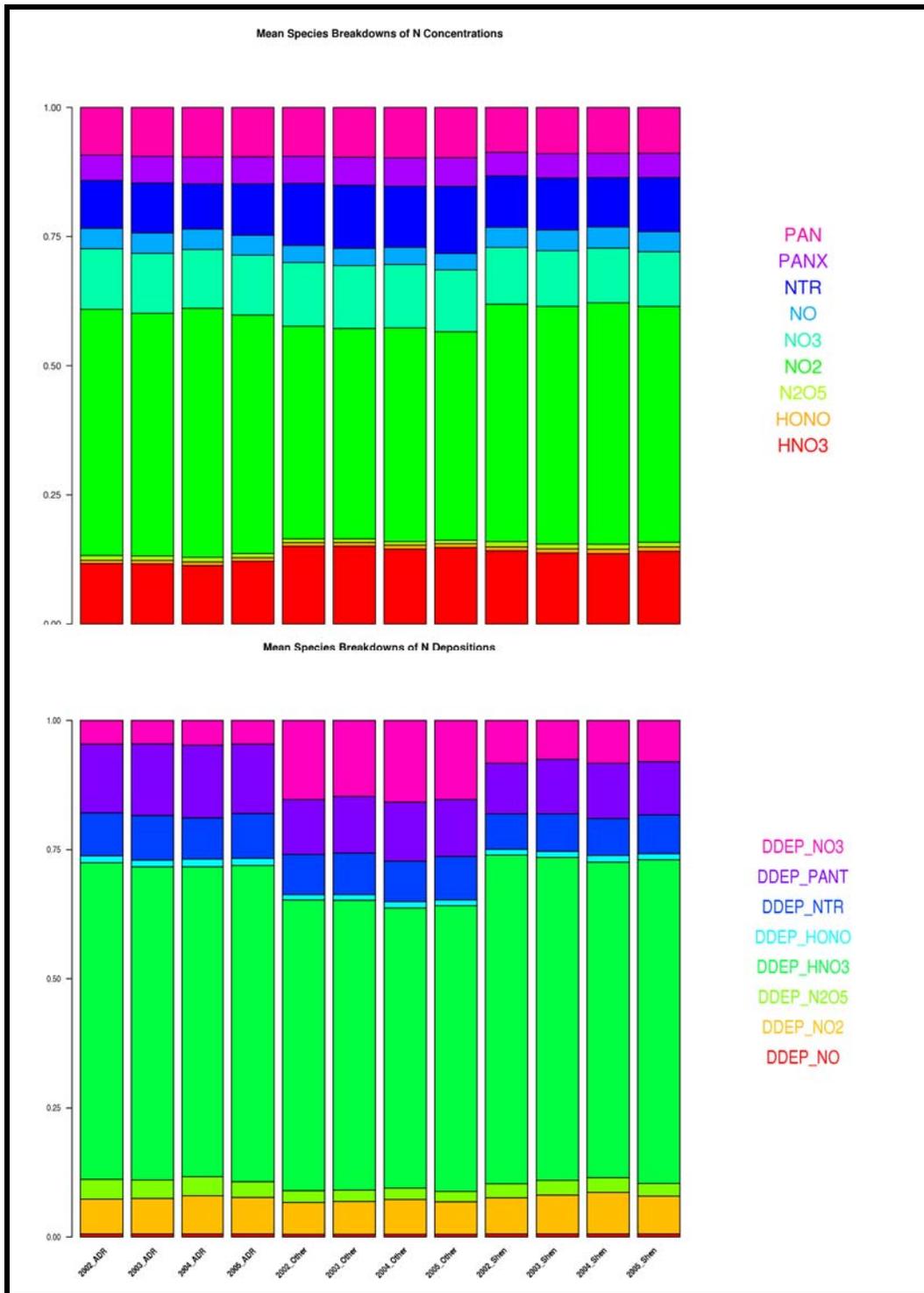
**Figure 8-1    Annual 2002 – 2004 CMAQ derived annual average fraction of ambient concentrations (above ) and deposition (below) of individual NOy species delineated by the Adirondack and Shenandoah case study areas and the remainder of the Eastern U.S. domain.**

14

1



Note: Oct. and Nov. NO₂ values are estimated.



Note: Jan. and Feb. PAN values are estimated.

2

**Figure 8-2**   Examples of the Relative Abundance of Several $NO_y$ Species Measured at Two Rural Southeastern Canadian Sites as a Fraction of the Total Measured $NO_y$ Concentration -- Kejimkujik, NS, (top) and Egbert, ON, (bottom) during 2003. Although both sites are in rural locations, the Kejimkujik, NS site represents more aged air masses as it lies considerably further downwind from major sources of NOx relative to the Egbert site. (*Source: NARSTO, 2010*)
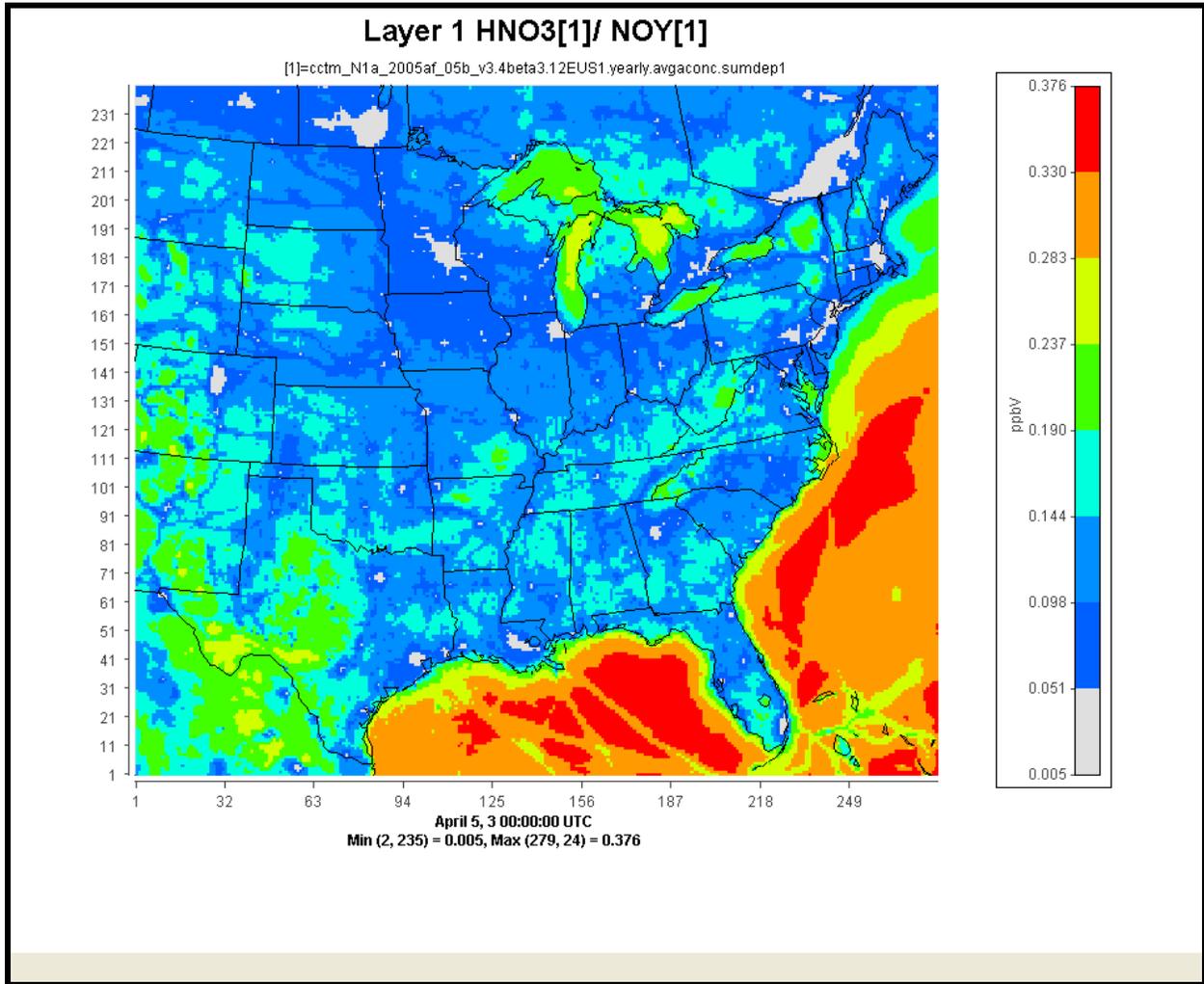
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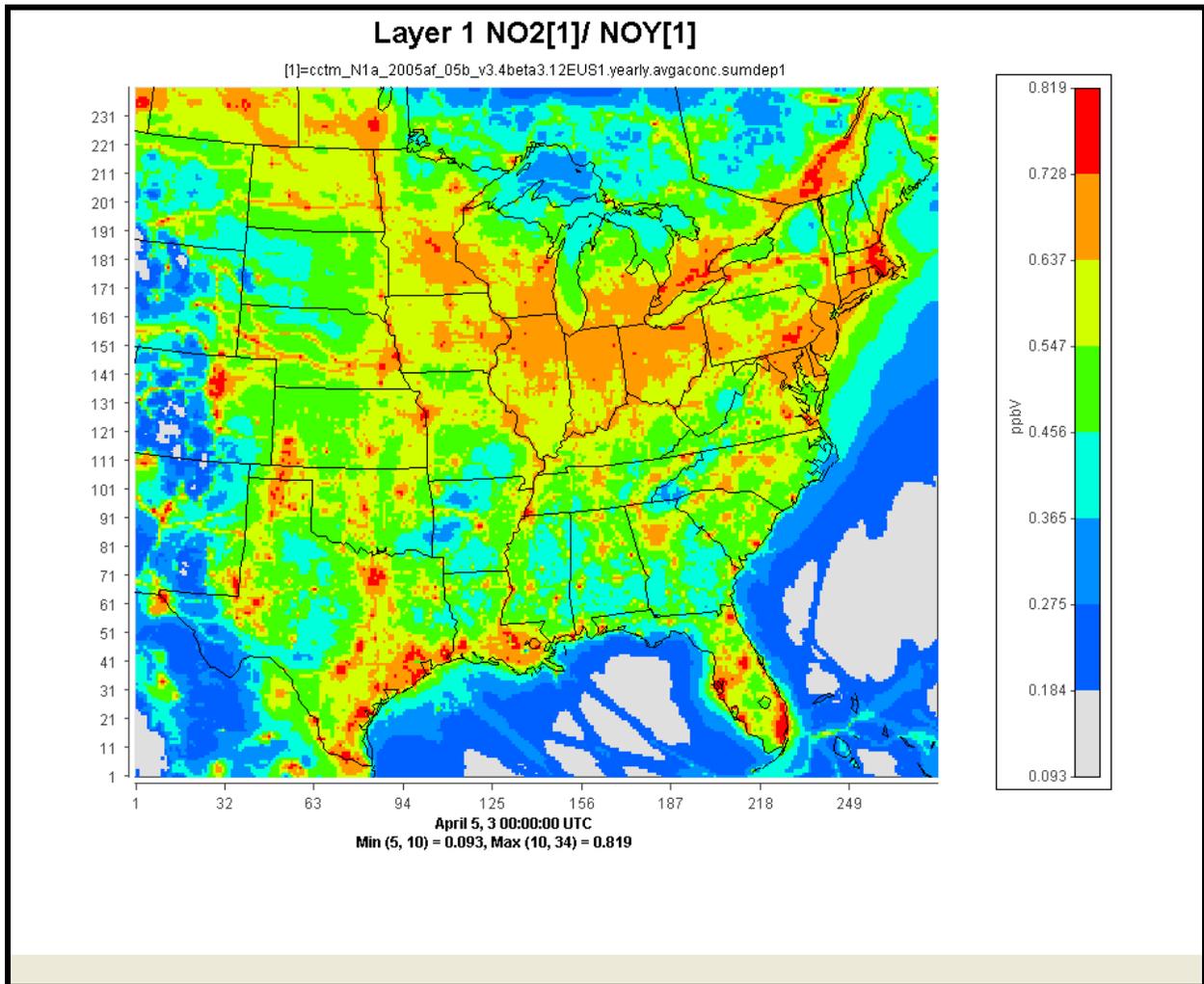
**Figure 8-3    Annual average fraction of NOy ambient air contributed by NO$_2$ based on 2005 CMAQ Eastern U.S. simulation at 12 km grid cell resolution.**

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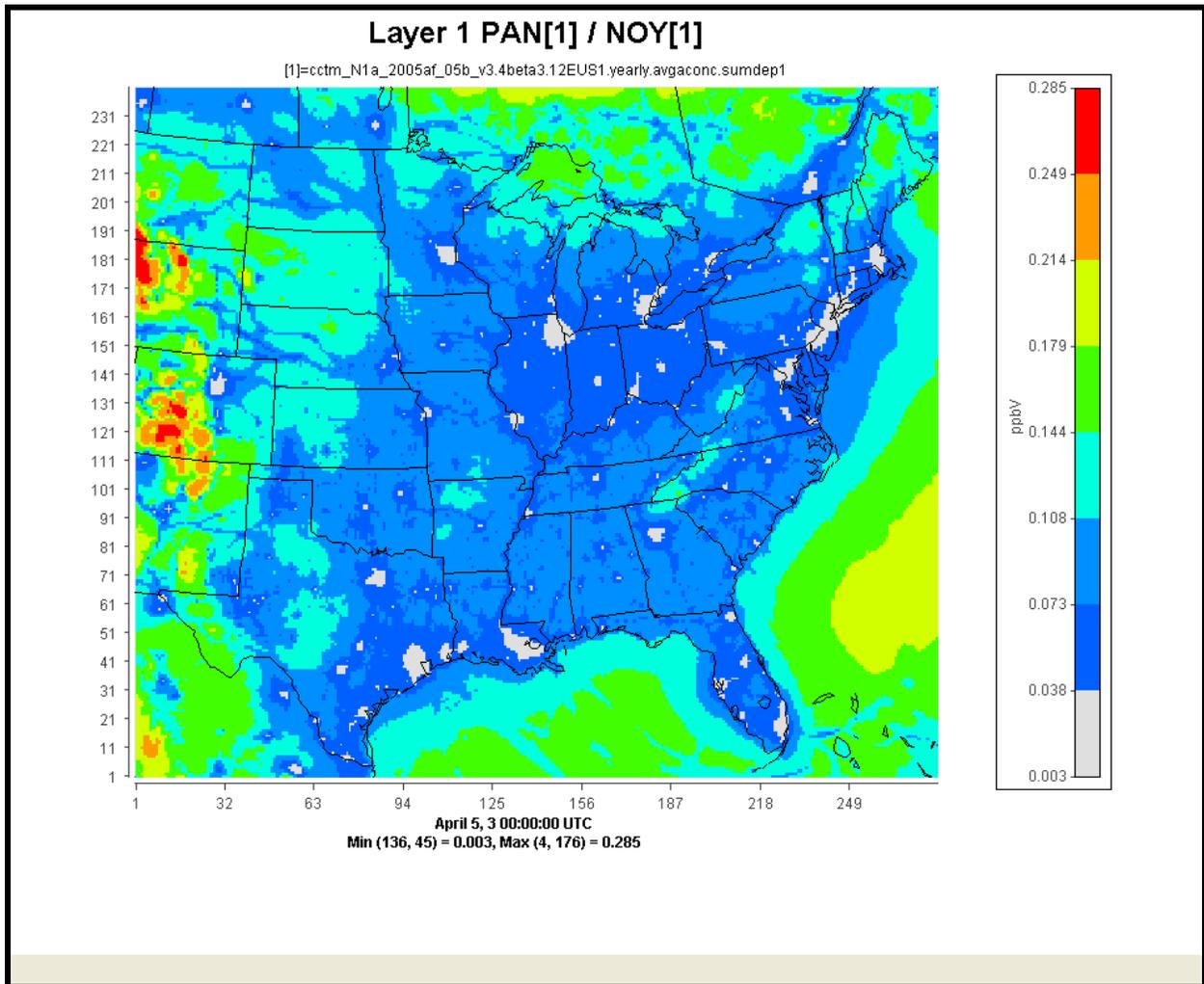
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**Figure 8-4    Annual average fraction of NOy ambient air contributed by HNO₃ based on 2005 CMAQ Eastern U.S. simulation at 12 km grid cell resolution.**

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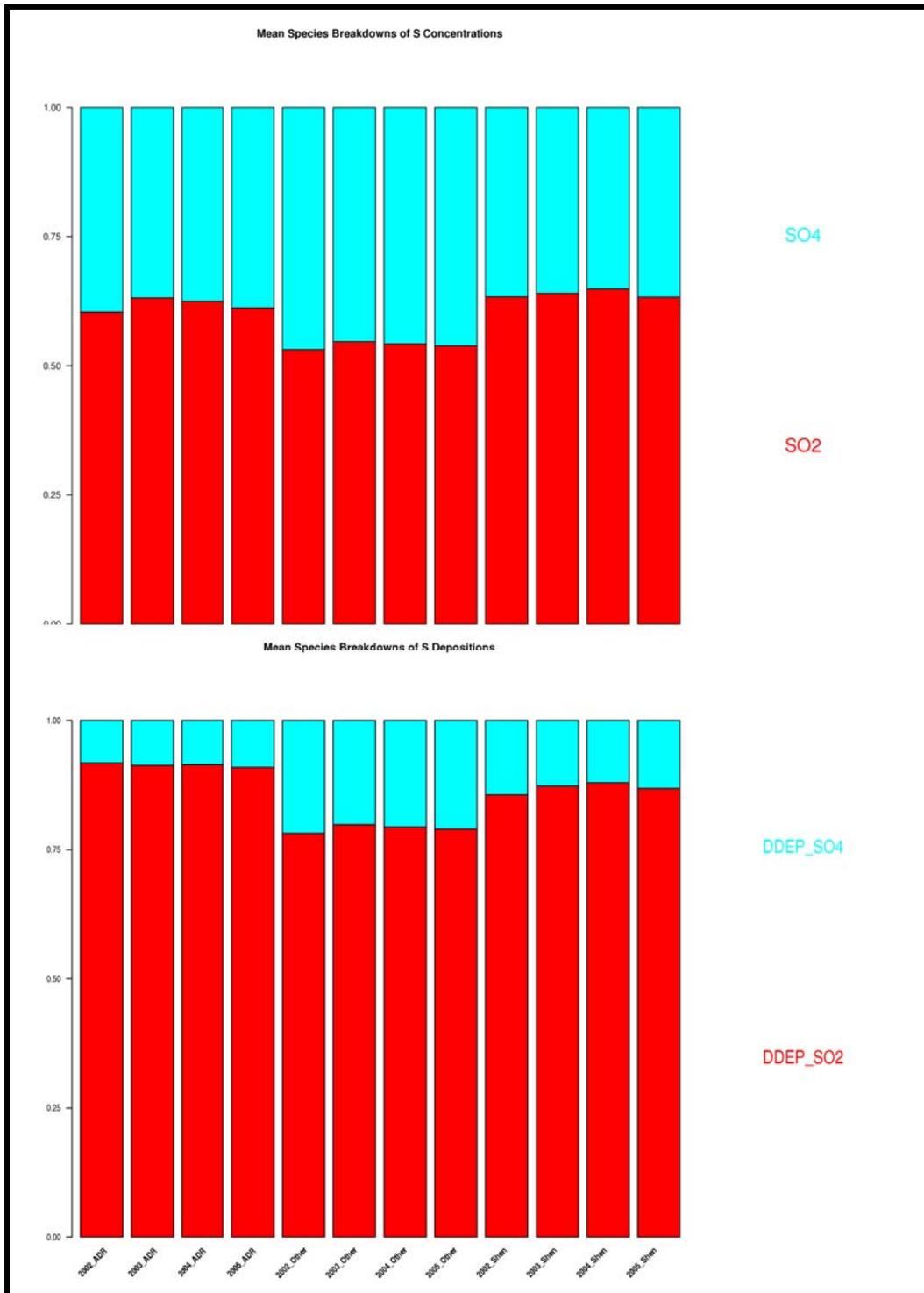
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Layer 1 PAN[1] / NOY[1]

**Figure 8-5** **Annual average fraction of NOy ambient air contributed by PAN based on 2005 CMAQ Eastern U.S. simulation at 12 km grid cell resolution.**

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7

**Mean Species Breakdowns of S Concentrations**

**Mean Species Breakdowns of S Depositions**

1

**Figure 8-6** **Annual 2002 – 2004 CMAQ derived annual average fraction of ambient concentrations (above ) and deposition (below) of individual SOx species delineated by the Adirondack and Shenandoah case study areas and the remainder of the Eastern U.S. domain.**

**2030 minus 2005 values in the Adirondacks**
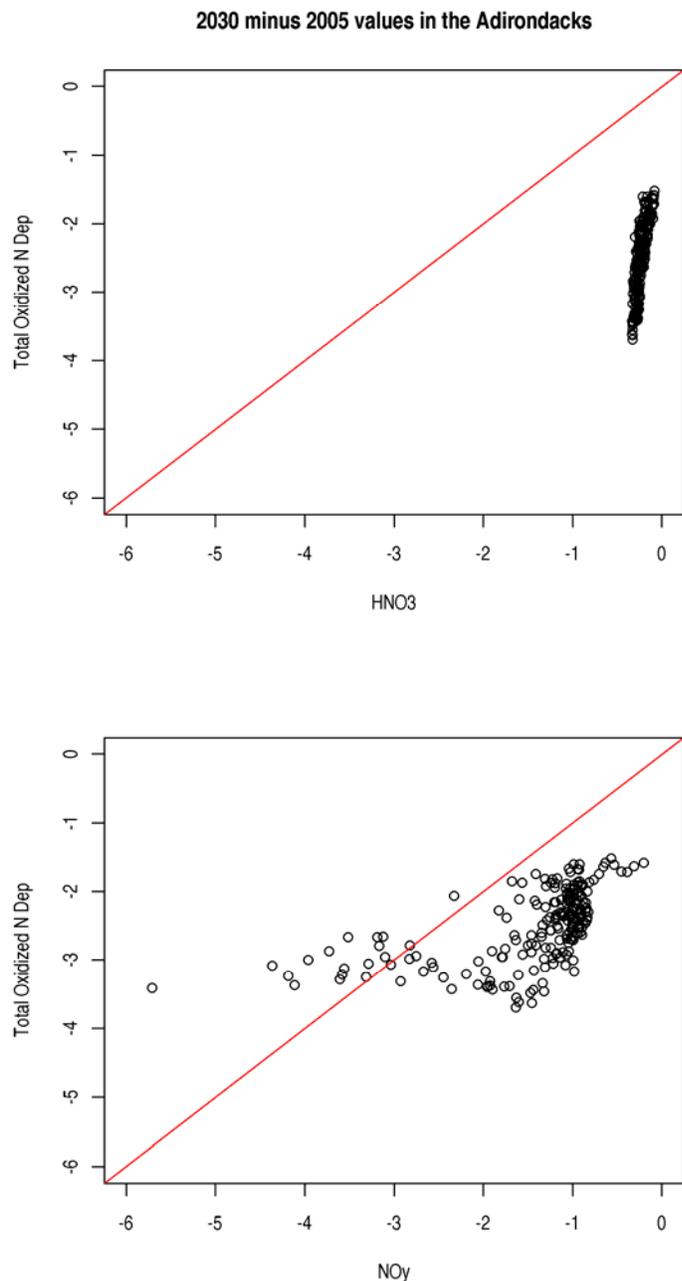




1
2    **Figure 7.**    Relationship of the change in total oxidized nitrogen deposition to change in ambient nitric acid (top)
3    and ambient NOy (bottom) based on changes in concentration and deposition fields associated with current (2005)
4    and reduced emission CMAQ simulations.    The values are based on the changes imparted for each 12 km grid cell
5    within the Adirondack region.    The emissions NOx and SOx emissions reductions of 50% and 42%, respectively
6    across the entire Eastern U.S.

7