Preliminary Comments from Dr. Daven Henze on 1 2 EPA's Policy Assessment for the Review of the 3 Secondary National Ambient Air Ouality Standards for 4 **Oxides of Nitrogen, Oxides of Sulfur and Particulate Matter** 5 (External Review Draft – May 2023) 6 06-27-23 7 8 9 Chapter 2 – Air Quality 10 11 To what extent does the Panel find that the information in Chapter 2 is clearly presented and that it provides useful context for the review? 12 13 14 The overview of SOx/NOx/PM sources, transport, and deposition is overall quite valuable and 15 useful in the context of the review. I've some minor comments and questions detailed below that 16 help clarify some aspects of the presentation. Outside of these, a larger overall question is why 17 satellite remote sensing based assessments of trends and distributions of sources and 18 concentrations of NO₂, SO₂, NH₃, and PM_{2.5} are not discussed more comprehensively (only NH₃ 19 is mentioned). I understand that such observations are, at present, not accepted as FRM or even 20 FEM. However, the information they provide on trends and spatial gradients does seem relevant, 21 in particular for construction and evaluation of components of the Nr deposition budget within 22 TDEP, parts of which (i.e., NH₃ dry dep) are based on CMAQ model estimates alone. 23 24 In a similar vein, it would be nice to see a bit more regarding NH₃ measurements and NH₄⁺ 25 concentrations. I recognize NH₃ is not a criteria pollutant. However, NH₃ is an unescapable and 26 critical component of understanding reactive nitrogen deposition. Figure 2-40 shows the 27 pronounced role of reduced N deposition in a majority of the area of CONUS. The discussion of 28 why PM_{2.5} is a good indicator of N dep (compared to aerosol nitrate) in Chapter 6 hinges upon 29 the role of NH₃. Thus, at a minimum it would useful to see analysis of NH₃ trends such as is 30 shown (Figs 2-31 – 2-34) for sulfate, nitrate, and PM, and inclusion of NH_4^+ in evaluation of 31 PM_{2.5} composition (Fig 2-26). 32 33 Specific comments on Ch 2: 34 2-2, Figure 2-1 and supporting text: The description of composition is a bit simplified. SO_4^{2-} isn't 35 the only PM form of sulfur oxides. S(IV) exists as $H_2SO_4(aq) + HSO_4^- + SO_4^{2-}$, dry aerosol can 36 contain NH₄HSO4 as well as (NH₄)₂SO₄, etc. The speciation can have important implications for 37 38 understanding PM trends (e.g., Silvern et al., 2017). Perhaps it should be noted that "sulfate" is 39 taken here to refer to all of these? Also, both nitrogen oxides and sulfate also lead to formation of 40 OC in PM via oxidation to form SOA. 41 42 2-3, line 20: N₂O₅ hydrolysis is the main pathway in winter — seems it warrants a more explicit 43 explanations than "via reactions with other oxidants and water." 44 45

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- 2-3, line 21: "Under the right thermodynamic conditions" is also rather vague. It's easy enough
 to say that cold, humid conditions help, along with availability of excess NH₃.
- 2-3, line 28: Reduced N is distinct from oxidized N, that's true, but this statement reads as if only
 the former contributes to PM_{2.5} and adverse deposition-related effects.
- 6

2-5, lines 5-6: This could more explicitly say that inventories are thus uncertain, and even state
estimated uncertainty ranges for different sources (e.g., SO₂ from power plants <20%, whereas
NOx from transportation up to 50%, NH₃ from all sources up to 100%...). These are mentioned
for NH₃ on page 2-12, which is good. Perhaps some discussion for uncertainties in sources of

- 11 other species would be good to include as well.
- 12
- 13 2-6/Fig 2-2: I was a little surprised that the NEI contains burning and soil emissions. Were these
- 14 generated by other models? For example, soil NO_x in CMAQ from modules like BDSNP or
- Rasool et al. (2019). Likewise, burning emissions are typically from inventories such as GFEDor FINN.
- 17

18 2-7/Fig 2-4: Regarding NO_x trends, there are several studies discussing these trends and

- suggesting that more recent decreases may be less severe. Also, no impacts of COVID-19
 lockdown are shown for spring 2020, even though these were known to significantly decrease
 transportation NO_x emissions (e.g., Harkins et al., 2021).
- 22

23 2-10: Line 4/5 states that NO₂ isn't directly emitted, which I don't believe is correct (though it is
24 emitted both as NO and NO₂, and rapidly interchanges). For example, O'Discoll et al. (2016)
25 report PEMS measurements of vehicle emissions for a set of diesel vehicles whose NOx

- $26 \qquad \text{emissions were } 44\% \text{ NO}_2.$
- 27
- 28 2-14: The section on NO, NO₂, and NO_x measurements is a bit jumbled and unclear. First,
 29 "direct measurement methods" is vague. Second, the "two step" process isn't clear (measurement
- 30 of NO is mentioned, but how about NO_x?). Next, the following sentence confusingly states that
- 31 chemiluminescent measurements detect NO, NO₂, and NO_x, though the previous sentence said
- 32 they don't detect NO₂. Further, the next few sentences discuss measurement biases, but it isn't
- clear how these are connected back to the previous issues of detecting only NO or NO_x (where
- 34 the latter is actually going to be NO_y). Lastly, it is noted on 2-40 that species such as HONO and
- 35 N₂O₅ have concentrations that are largest near sources and in urban areas, somewhat in contrast
- 36 to 2-14, line 9, which states that urban concentrations of interfering species are relatively small.
- 37
- 2-16/17: It seems PM₁₀ measurements should be mentioned somewhere, either within 2.3.3 (PM_{2.5} measurements) or 2.3.4 (other).
- 40
- 41 2-29: Figure 2-26: Why not include NH_4^+ from NCore and CSN sites? These could perhaps be
- 42 distinguished in some way from the IMPROVE sites, which don't have NH_4^+ ?
- 43

2-37/38: The differences between the process shown for constructing the TDEP dry dep between 1 2 Fig 2-36 and 2-37 are a bit distracting. Why not make one figure with the detailed version? Also, 3 the detailed version omits "other species" as estimated by CMAQ. 4 5 2-40, line 30-32: Regarding the reason for not bias-correcting TDEP NH₃ -- NO_x is also highly 6 spatially variable, perhaps as much as NH₃. Thus, I think it would be more precise to say here 7 something like owing to the relative paucity of NH₃ observations. 8 9 2-41, line 5: The example on model biases for dry and wet deposition having a compensating 10 effect when considering total deposition is true, but doesn't seem particularly relevant given that 11 the model (CMAO) is used only for bias correction of the dry portion of the TDEP estimate, 12 whereas the wet portion is determined empirically (Fig 2-36). Thus, wouldn't a high bias for dry 13 dep velocities lead to a high bias in total deposition? 14 15 2-45, lines 8-10: NO_x is also from natural sources like fires and lightening; natural NH₃ is also 16 from fires. 17 18 2-45: It's not clear what is meant by relatively short lifetime (hours? days?), but in this context it 19 seems important to distinguish between the gas-phase lifetime (hrs) and the particulate phase 20 lifetime (days). 21 22 2-50 and Fig 2-43: Were NH₃ emissions held constant for these simulations, or, more 23 realistically, did they continue with a slight increasing trend? 24 25 26 Chapter 6 – Relationships of Deposition to Air Quality Metrics 27 28 To what extent does the Panel find the investigation of relationships between air concentration 29 and deposition to be technically sound and clearly communicated? What are the CASAC views 30 on the consideration of key limitations and associated uncertainties? 31 32 Overall, there is a need to introduce more stringent standards, as indicated by the administrator's 33 prior judgement that current standards do not adequately provide protection against adverse 34 deposition-related effects. The coupling to the primary PM_{2.5} standard of 12 ug/m³ would be a 35 tightening, while conveniently sustaining the practice of mitigation of welfare effects through 36 primary standards. A concern is that reliance on PM_{2.5} concentrations as an indicator could lead to situations where the "wrong part" of the PM_{2.5} is reduced to attain the primary standard, from 37 38 the perspective of reducing N deposition, especially as reduced nitrogen is an increasingly large 39 component of N deposition yet NH₃ emissions are not regulated. Scientifically, it would be more 40 direct to target N deposition values themselves as an indicator, which is perhaps permissible 41 within the CAA's definition of a "level of air quality." That being said, below are my specific 42 comments with regards to this question and the reviews approach to quantifying the relationships 43 between air concentrations and deposition.

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6-7, lines 25-33: Why not separately consider wet oxidized and reduced N (rather than total)
deposition vs IMPROVE sulfate, nitrate and PM_{2.5}? This could help explain why they don't find
a robust relationship between nitrate and total wet N deposition.

Figs 6-4, 6-5, 6-9: Overall I find these matrices very interesting and helpful, but they also take a
while to absorb and are tricky to compare. In particular, they could be improved to help support
the use of PM_{2.5} as an indicator for N dep. Here are a few things that would help:

8 9 Similar to my comment above for 6-7, evaluating oxidized vs reduced N deposition 10 would be useful. 11 The modeled vs measured matrices would be much easier to compare if ordered -12 similarly, including the same quantities first (i.e., S + N deposition, N, NH_4^+ ,...). The same even applies just between Figs 6-4 and 6-5 (where e.g. the order of NADP NH_4^+ 13 14 and NO_3^- are swapped). 15 There is a lot of variability in measured N dep not explained by aerosol nitrate or 16 nitric acid alone; the clear omission is NH_x. Can comparison to AMoN NH₃ be 17 considered from measurements? 18 To help address the previous point, a useful addition to the model matrix (Fig 6-9) 19 would be NH_3 (g) and aerosol NH_4^+ , and for consistency with the measured matrices 20 it would also be good to include PM_{2.5}. This is important as the combination of these would allow us to better understand the role that ammonia plays on PM_{2.5} as an 21 22 indicator of N deposition, which contributes to the suggested use of PM_{2.5} as a 23 standard in this regard. 24 There are several panels that seem to exhibit two distinct regimes (Fig 6-9) or -25 bimodal relationships (6-4, 6-5) — it would be interesting to examine the data more, 26 perhaps by location, to evaluate why these occur. It does seem that Fig 6-12 and 6-13 27 address the former perhaps, showing the time dependence may lead to the different 28 clusters. 29 - The scales are quite different for NADP S (up to 50) vs CMAQ wet dep S (up to 12) 30 — what is the reason for this? Is the model low by more than a factor of two? In 31 contrast, NADP N and Total Dep N from CMAQ are the same scale. 32 33 Regarding the definition and use of EAQM: I appreciate the approach, and the review well 34 demonstrates the value compared to just considering concentration levels in an eco-region, in 35 terms of an air concentration indicator that is better correlated to deposition. That being said, I 36 have several questions and concerns: 37 38 -The threshold of 1% for a site being considered representative seems low. The time of 39 48 hrs also seems low, given the role of secondary species and PM with lifetimes of 40 2-10 days. These issues are later recognized in discussion of uncertainties in 6-42. 41 However, actual sensitivity studies should be presented to evaluate the robustness of 42 the relationships between deposition and EAOM values with regards to these 43 assumptions. 44 The EAOM approach based on HYSPLIT (meteorological trajectories that neglect 45 chemistry) could miss situations where an emission of e.g. SO_x or NO_x in one

1	location could reduce deposition at a location downwind (by promoting secondary
2	PM formation that travels further than the target area). We've shown the role of
3	chemistry in such situation in our previous work evaluating source contributions to
4	reactive nitrogen deposition in biodiversity hotspots (Paulot et al., 2013) and Federal
5	Class I regions (Lee et al., 2016). I'm not saying that this type of highly non-linear
6	behavior dominates, this is an extreme case, but I do think that in general, chemistry
7	and thermodynamics shouldn't be neglected when considering air / deposition
8	relationships.
9	- A lot of Nr transport and dep will be seasonable, because of the seasonal nature of
10 11	over the entire year may not be indicative of the transport patterns during the
12	"deposition season." This would be another thing to consider via sensitivity
13	calculations.
14	
15	Fig 6-14, 15, 17 and 18 — it seems the relationship is very weak for the most recent two time
16	periods. While this approach may work historically over the past two decades, it's not clear that
17	below S dep levels of e.g. 5 kg S/ha yr there is a strong overall relationship across all sites. The
18	text though does mention this in several places. However, I'd also note that placing the statistics
19	(r) referred to in the text directly on the plots would be useful.
20	
21	Fig 6-25: This is a rather remarkable figure, and to be honest I'm somewhat skeptical regarding
22	the lack of scatter. I understand that PM _{2.5} will capture both reduced and oxidized N. If that's the
23	explanation for this very high correlation, it could have been tested in earlier sections by
24	considering more evaluation with NH ₃ , NH _x , and oxidized vs reduced N deposition. Regardless,
25	there is still a large fraction of PM _{2.5} mass that is not associated with N of any kind (as shown in
26	Fig 6-24), which makes the very tight correlations shown here difficult to believe. It is also
27	concerning, in terms of a standard, for cases where PM _{2.5} exceedences above 12 ug/m ³ are driven
28	by non S or N rich sources, such as carbonaceous PM from wildfires.
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31	Editorial
32	
33	1-9, 14: Typo — extra "10"
34	
35	2-2: Note that section 2-3 begins with a quick overview of NOx sources, where here the intro to
36	SOx does not discuss sources.
37	
38	2-2/2-3: The following two sentences are repeated verbatim in two consecutive paragraphs: "Dry
39 40	depiction is an importantAlthough particulate sulfate"
4U 1	2.2. Why is y of NOY subscript but y of SOy is got? Some like it should be fart at MU-
41 17	2-3. Why is a of NOX subscript but a of SOX is not? Seems like it should be, for both. NHX was
+∠ ∕\3	also given a subscript x.
+J	

2-19: For Fig 2-15, the "dropped pin" marker isn't the greatest, as it's hard to tell where many
pins touch. I'd suggest a plot more like Fig 2-14. The same applies to Fig 2-17, though to a lesser
extent.
2-23: Does the 80 ppb on line 10 refer to the max or the actual design value, i.e., the 98th
percentile? The text is a little unclear, but caption of Fig 2-18 says 98th percentile.
2-29, line 13: to be

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- 10 2-42: proxy) 11
- 12 2-44: within in
- 13 14 2-44: the each
- 16 6-3, line 1: Near ground-level, rather than for ground-level?
- 18 6A-1: three separate pollutants
- 2021 References
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