

**\*\*Author Responses to comments are in Red**

This manuscript describes trends in sulfate and nitrate concentrations measured from 1990-2011 at Barbados, as well as other species such as dust and ions. Nitrate was found to have changed little over the decades examined, while sulfate decreased and then started to increase around 2000. Modeled sulfate from the CMAQ-EQUATES model did not show similar trends, and a model-observation bias in sulfate was reported. Back trajectory analyses suggest that high concentrations of nitrate were associated with transport of biomass burning from Africa. The long record of measurements at Barbados are critical for understanding changes in global emissions of pollutants, and comparisons to model results are useful for understanding observations, as well as identifying potential biases within the model. This paper is fairly well written, however there are some potential issues and questions with some analyses which are described as part of the comments listed below. I recommend publication after addressing comments and updating the manuscript.

We thank the reviewer for the helpful comments.

Line 18: Does this nitrate concentration reflect an average over this entire period? Does the 0.04 ug/m<sup>3</sup> reflect a standard deviation or uncertainty?

We have now specified that this nitrate concentration reflects an average, with its associated standard deviation, over the entire period except for during the outliers in 2008 and 2010.

Line 18 and onward: Please use the micrometer symbol for concentrations.

The change has been made.

Line 21: It would help to list the years over which this reduction is true.

We have now specified the date range.

Line 22: Include end date here (e.g., from 2000 through 2011).

The change has been made.

Line 23: The time frame here is 1990 and later? How do these levels correspond to pre-1990?

While our dust mass concentration measurements go back in time before 1990, corresponding mass concentrations of sulfate and nitrate do not.

Line 51: This is unclear. Are the authors implying that emission inventories are lacking at observation sites?

We have changed lines 50-52 to now read, "In turn, comparing the EQUATES model output to our time series provides guidance on where in-situ measurements are needed that would improve emissions inventories and measurement-model agreement."

Line 71: Both "U.S" and "US" are used- check text for consistency.

The change has been made.

Line 80: Define "EU"

EU has been defined.

Line 89: What about fires in the U.S. and Canada, such as those that influenced the eastern U.S. in 2023?

Prescribed burns in the southeastern U.S. could also impact our measurements in Barbados.

We now state on Lines 104-105, "Prescribed burns in the southeastern U.S. in winter and spring may also contribute biomass burning emissions to the aerosol burden observed in Barbados (Nowell et al., 2018)."

Line 122: What is the size-cut of these measurements? How long are samples collected?

We now state on Lines 132-135, "The upper particle size limit for our filter collection method is approximately 80-100 $\mu$ m or greater based on the geometry of our sampling rain hat (Barkley et al., 2021). Filters were collected daily (e.g., every 24 hours); however, a few multiday samples were also collected that typically span 2 days."

Line 135: Have any changes of these measurements occurred over this period that could influence trends? Why are data after 2011 not included?

The only change over this period is the addition of the flame photometer after 2004 allowing cation analysis beyond sodium after this period. The analysis of anions did not change over this period.

Ion chromatography analysis stopped after 2011 and has just recently resumed with a new instrument.

Line 135: Include statements of how trends are calculated? Are they simple OLS regression? How is statistical significance determined?

Trends presented in this work were derived from ordinary least squares regression, but we decided to increase the robustness of our findings with Theil-Sen regression, which did not change our trends and outcomes significantly. Significance is calculated using paired samples t-tests. This is now stated in the manuscript.

Line 151: How are concentrations below minimum detection limits dealt with?

We now state on Lines 178-179, “Filter samples with undetectable amounts of dust and soluble ions compared to procedural blanks are removed from our analysis.”

Line 178: I assume the ‘unexpectedly increased’ is referring to observations, not model?

Correct. We have clarified this point in the text.

Line 179: Line 166 says model is available from 2002 through 2019?

Correct. Our observations span 1990-2011 and the EQUATES model overlaps with our observations from 2002-2011; however, the model product is available up to 2019.

Line 184: Does the model predict ions or total sulfate, nitrate, calcium, etc.? What is the size range of the model output?

The model predicts total sulfate, nitrate, etc. rather than ions. The size range is up to  $PM_{2.5}$  for fine mode aerosol and  $PM_{10}$  to  $PM_{2.5}$  for coarse mode. We added both fine and coarse mode aerosol to compare with our filter observations at Ragged Point.

We now clarify the size ranges as well as the species simulated on Lines 203-205, “Simulated concentrations of aerosol sulfate, nitrate, calcium, potassium, and sodium were obtained for fine mode aerosol (e.g., Aitken and accumulation mode, PMF model outputs) and coarse mode aerosol (Total PM –  $PM_{2.5}$ , PMC model outputs).”

Line 184 and 189: Ions are written both as their chemical symbols and as words- check paper for consistency.

We have made the change.

Line 194: Does the crustal abundance of  $Ca^{+2}$  refer to North Africa?

Yes. We have also added another reference specific to Northern African soils in the text.

Line 208: What year does “goes back in time far enough” refer to?

We now specify that the NCEP reanalysis product extends back to 1990 at the beginning of our dataset.

Line 210: Examine trends in what?

We have now specified that we examined trends in air mass back trajectories.

Line 213: The section titles don't need the results of the section included and can be simplified.

We have simplified our section titles to remove the results.

Line 226: What were trends in dust?

We now specify that dust had no yearly average trend over our 1990-2011 record and show the trend in Figure 2. Lines 299-300 now state, "annual average measured dust mass concentrations are also shown in Fig 2 and show no appreciable increase or decrease from 1990-2011 ( $R^2=0.06$ )."

Line 233: Trends in what? Perhaps replace this with "concentration" since different years in each site are being considered, and so trends are difficult to compare.

We have taken this suggestion and replaced "trends" with "concentrations."

Line 237: For additional comparisons/validations to the Barbados results, consider sulfate and nitrate data over the same periods from the IMPROVE site in Virgin Islands.

We now provide some comparison to the IMPROVE site in the U.S. Virgin Islands, which shows a lack of a trend in nss-sulfate.

We now state on Lines 292-297, "Also, the trend in nss-sulfate at Barbados differs from long-term observations measured at an IMPROVE site in the Virgin Islands. Sulfate shows no trend from 2004-2021 (Hand et al., 2024). The difference in trend in nss-sulfate between Ragged Point and the IMPROVE site in the U.S. Virgin Islands is likely due to more influence from the U.S. and less influence from African emissions. Further, the IMPROVE site does not follow a sector-controlled sampling protocol as does the site in Barbados."

Line 249: Same comment as above: what are the trends in dust.

We now specify that dust annual trends show no yearly trend over time ( $R^2=0.06$ ).

Line 250: What is the correlation coefficient between nss-sulfate and dust?

We now specify that the correlation coefficient between annual average dust and nss-sulfate mass concentrations was  $R^2=0.001$ .

Line 315: Can the section title be generalized? It seems to include three very different topics.

We have changed the section title to “**Trends in Non-Sea Salt-Sulfate and Emissions of SO<sub>2</sub>**”

Line 318: Line 320 suggests that that not all seasons show this behavior (not winter).

We have adjusted the sentence to state that trends in sulfate were observed during almost all seasons.

Lines 382-388 now read, “Figure 3 reveals that the decrease in sulfate and subsequent increase are measured during most seasons. Table 1 further provides correlation coefficients and the rate of change in either nitrate or sulfate in  $\mu\text{g m}^{-3}\text{yr}^{-1}$  for data collected pre- and post-2000 when the trend in nss-sulfate changed. Pre-2000, nss-sulfate shows a consistent decline in each season with the weakest decline in winter and the strongest reduction measured in JJA at  $-0.036 \mu\text{g m}^{-3}\text{yr}^{-1}$  ( $R^2=0.72$ , Table 1). Post-2000, nss-sulfate increased during every season with comparable increases in every season. In JJA, nss-sulfate increased at  $+0.028 \mu\text{g m}^{-3}\text{yr}^{-1}$  ( $R^2=0.61$ , Table 1).”

Line 352: The caption states that Figure 6 shows concentrations but the y-axis shows percentage change. I suspect this is done to plot emissions and concentrations on the same axis but perhaps have a secondary y-axis so actual concentration and emission values can be shown? Or change the caption and describe the % change in the text. How was % change calculated? Relative to what?

We have changed the caption for Figure 6 to read:

**Figure 6:** Percent changes in NSS-Sulfate mass concentrations measured at Ragged Point from 1990-2011 are shown in red. NSS-Sulfate mass decreases from  $0.87 \mu\text{g}/\text{m}^3$  in 1990 to  $0.64 \mu\text{g}/\text{m}^3$  in 2000 and subsequently increases to  $0.90 \mu\text{g}/\text{m}^3$  in 2011. The data are normalized to the maximum NSS-sulfate mass concentration,  $0.92 \mu\text{g}/\text{m}^3$  measured in 2010. The percent changes in emissions of sulfur dioxide (SO<sub>2</sub>) from the CEDS emissions inventory from McDuffie et al., 2020 are included for comparison. Decreasing emissions of SO<sub>2</sub> from the U.S. and EU are shown in blue lines. U.S. SO<sub>2</sub> reduces from 21.12 to 5.85 Tg S/yr and EU SO<sub>2</sub> reduces from 28.06 to 7.74 Tg S/yr. Percentages are calculated by normalizing to the maximum values in SO<sub>2</sub> emissions observed in 1990 for both the U.S. and EU. SO<sub>2</sub> emissions from Africa increased from 4.13 to 5.95 Tg S/yr; they are normalized to the maximum SO<sub>2</sub> emissions observed in 2010 at 6.16 Tg S/yr.

Line 361: Was only one model grid used to represent Ragged Point? Are the surrounding model grids consistent in concentration values?

One grid was at Ragged Point while the remaining 15 grids were used to represent the area to the east of the site to minimize influence from local emissions. The surrounding model grids are consistent in concentration values.

We now clarify the model grids used in the Methods section of the manuscript (Lines 199-203), "Species predictions were extracted from the lowest CMAQ model layer (~10m in thickness) for a source area over the Atlantic Ocean to the east of the island from 59.5627°W to 56.5448°W longitude and 14.3989°N to 11.4566°N latitude (equivalent to 16 grid cells with one cell over Ragged Point and the others to the east of the site)."

Line 362: It seems like Figure S5 shows Na, not dust? Figure S6 shows dust.

The paper has been rearranged. Sodium is shown in Figure S1 and dust in Figure S2.

Line 367: Typo: Dessert

The typo has been fixed.

Line 369: Can the authors provide more information on nss-sulfate estimates from the model? Were these determined from modeled sodium (I see this is referred to in the figure 8 caption- perhaps include in the text)?

The Methods section includes information on how modeled nss-sulfate estimates were calculated on Lines 207-213, "Because aerosol filters collected at BACO capture total suspended particulate matter, model outputs of fine and coarse mode aerosol concentrations were combined (e.g., PMF + PMC model outputs) to give total aerosol mass concentrations of sulfate, nitrate, sodium, potassium, and calcium. Total concentrations of nss-sulfate and nss-potassium were calculated using Equations 2 and 3, respectively, and model outputs of total sodium mass concentrations, total sulfate mass concentrations, and total potassium mass concentrations from combined coarse and fine mode aerosol model outputs."

Figure S5 shows sodium concentrations that are 2-3 times higher than observations. How much uncertainty is in modeled nss-sulfate based on the difference in these measured and modeled sodium values?

If we scale the model bias in the sodium to our observations, then the agreement between our observations of nss-sulfate and model estimates becomes even worse. This is because the high bias in sodium is due to a high bias in sea spray, which also includes sulfate. Further, the bias in nss-sulfate decreases over time while the bias in sodium is constant over time. Therefore, the bias in nss-sulfate is likely due to either the sources of sulfate (other than sea spray) or the conversion of SO<sub>2</sub> to sulfate.

We have now stated on Lines 469-473, "The model overpredicts nss-sulfate in the earlier years (2002-2007) then converges closer to our measurements at Ragged Point after 2008 as

shown in Fig 7. Because trends in sea salt (e.g., sodium from EQUATES, Figure S1) show a constant high bias in all years, the overprediction of nss-sulfate reflects biases in sources of sulfate (other than sea spray) or biases in the conversion of SO<sub>2</sub> to sulfate.”

Line 373: These percentages are the % relative to total? What years do these values refer to?

The percentages are relative to the total modeled nitrate and are averages for all years, which we now specify in the paper.

We also point out that the amount of modeled fine nitrate was elevated in MAM of 2010, when enhanced nitrate was also observed in our measurements and attributed to African biomass burning, on Lines 439-445, “EQUATES predicts nitrate concentrations in fine and coarse aerosol sizes. A greater proportion of fine nitrate is predicted in DJF (40% of the total modeled nitrate) and MAM (26% of the total modeled nitrate) during all years compared to JJA and SON (18% of the total modeled nitrate for both seasons, see Fig S8). This seasonality is likely due to increased contributions of nitrate from fine biomass-burning aerosol produced in Sub-Saharan Africa north of the equator in winter and spring. This point is highlighted in MAM of 2010 when the amount of modeled fine nitrate was elevated (35% of total modeled nitrate).”

Line 387: Were daily data used to calculate performance evaluation statistics?

Monthly data were used to calculate performance evaluation statistics. We now clarify this point in the paper.

Line 389: Define SI.

SI has been defined as Supporting Information the first time the SI is referenced in the paper.

Line 391: And 2005 (greater than 20%)

We have now added the fact that 2005 had a NMB greater than 20% for nitrate.

Line 394: What trend are the authors referring to?

We now specify that this is the trend of the model overpredicting nss-sulfate from 2002-2007.

Line 395: Typo: beings

We have fixed this typo.

Line 402-402: What are the implications for non-US emissions in CMAQ?

We now more explicitly state on Lines 483-484, "This overestimate in declining sulfate in the U.S. may mask trends (including stronger increases in sulfate) in other regions."

Line 406: What does "filter observations were limited" mean?

We have now clarified that filter measurements were not collected starting in January and ending in May of 2002.

Line 408: include "model" here when referring to the high concentrations.

The change has been made.

Line 416: What level of the model does SO<sub>2</sub> refer to? What does "region near Barbados" mean (line 417).

The modeled SO<sub>2</sub> is from the same region as the particle phase data. This has been clarified in the Methods section of the paper on Lines 200-203, "Species predictions were extracted from the lowest CMAQ model layer (~10m in thickness) for a source area over the Atlantic Ocean to the east of the island from 59.5627°W to 56.5448°W longitude and 14.3989°N to 11.4566°N latitude (equivalent to 16 grid cells with one cell over Ragged Point and the others to the east of the site)."

Line 416: This analysis supposes that the sulfate oxidation is happening near the Barbados site, not necessarily that the sulfate has been transported. Is that a realistic assumption? Are there many sources of SO<sub>2</sub> on Barbados? If not, it has to be assumed that the SO<sub>2</sub> is transported to the site as well? The same assumptions are true for H<sub>2</sub>O<sub>2</sub>?

We agree with the reviewer's point here. The lifetime of SO<sub>2</sub> and other oxidants is short compared to the 5 to 7-day transport time of these emissions to our site from Africa. We have now amended the text to state that our oxidation ratio calculations primarily account for the conversion of locally emitted SO<sub>2</sub> to sulfate but most of the nss-sulfate observed is likely due to long-range transported sulfur that is converted prior to transport to our site.

We now state on Lines 496-504, "We note that because the lifetime of SO<sub>2</sub> is predicted to be ~20 hours and as much as ~40 hours depending on the latitude of the source of SO<sub>2</sub> and the season (Green et al., 2019; Lee et al., 2011), our oxidation ratio estimates here are most relevant for local emissions, including sulfur emitted from marine phytoplankton (e.g., DMS). However, prior measurements at Bermuda suggest a longer lifetime for long-range transported SO<sub>2</sub> compared to local oceanic emissions from DMS, which are subject to strong condensational losses to sea spray in the marine boundary layer (Keene et al., 2014). As such, long-range transported sources from Africa, the U.S., and EU have likely been converted to sulfate upwind



of Barbados and SO<sub>2</sub> concentrations shown here most likely reflect oceanic sources though some contribution from long-range transport is also possible.”

Line 425: Since the oxidation ratio is calculated with modeled SO<sub>2</sub> and measured nss-SO<sub>4</sub>, can the authors describe how they accounted for the model bias in SO<sub>4</sub> and its potential influence in the oxidation ratio? For example, without SO<sub>2</sub> measurements, it is hard to say whether there is a bias in SO<sub>2</sub> in the model, however, given the bias in nss-SO<sub>4</sub>, it's possible and perhaps likely that there is also a bias in SO<sub>2</sub>. Doing a ballpark calculation based on the reported mean bias in Table S1 and the oxidation ratios shown in Figure 9, the correlation between the mean bias and the oxidation ratio is  $r = -0.7$ . Have the authors calculated the ratio with the modeled nss-SO<sub>4</sub>? Using eyeballed-values of the nss-sulfate concentrations from EQUATES in Figure S8 and the SO<sub>2</sub> in Figure 9 to calculate the oxidation ratio, the correlation for the change in the modeled oxidation ratio over time is  $r=0.18$ . While it's possible that the oxidation ratios in Figure 9 are real, the authors need to provide more evidence that the model bias is not influencing these estimates.

The reviewer is correct here that it is possible that there is a bias in modeled SO<sub>2</sub> that would influence our oxidation ratios calculated in this work. We have changed the text in this section of the paper to reflect this bias as well as the fact that this exercise is really examining local trends rather than changes in long-range transported SO<sub>2</sub>, which is likely to already be in the form of sulfate before arriving to our site.

The text on Lines 507-511 now reads, “We note that the predicted oxidation ratios are likely an overestimate because EQUATES overpredicts nss-sulfate compared to observations and the overprediction decreases with time. As such, the increase in the oxidation ratio, which is small from Figure 9, likely has a minimal influence on the observed trends in nss-sulfate observed at our site.”

We have also removed mention of the oxidation ratio in the abstract.

Line 439: Define RH

We have made the change.

Line 444: The evidence related to the influence of anthropogenic emission impacts on trends could be strengthened. Without knowing the behavior in benzene or CO prior to 2002, it is inconclusive to state the role of the anthropogenic emissions influencing Barbados since it is unknown whether they were increasing before 2002?

We now provide a stronger argument in the prior section where we compare emissions of SO<sub>2</sub> from Africa with our observations of nss-sulfate. We now point out the lack of trend in SO<sub>2</sub> emitted from Africa prior to 2000 and a steady increase post-2000 that matches our record of nss-sulfate. We also include a figure in the SI that shows that EQUATES predicts an increase in SO<sub>2</sub> from anthropogenic emissions from Africa from 2002-2011.

The text on Lines 409-421 now reads, “Figure 6 also compares the trends of nss-sulfate observed at Ragged Point to increasing emissions of SO<sub>2</sub> from Africa (McDuffie et al., 2020). Before 2000, SO<sub>2</sub> emissions from Africa oscillated around 4.44±0.19 Tg S/yr but show no consistent trend (R<sup>2</sup>=0.027). However, after 2000, emissions of SO<sub>2</sub> from Africa steadily increase by 37% from 2000-2011 (4.33 Tg S/yr in 2000 and 5.95 Tg S/yr in 2011, R<sup>2</sup>=0.88). The rate of increase in SO<sub>2</sub> is on par with the rate of increase in nss-sulfate of 29% observed in Barbados suggesting that anthropogenic emissions from Africa are affecting the nss-sulfate trends measured in Barbados.

We next utilized the CMAQ model results from EQUATES to gain further insight into the observed recovery of nss-sulfate (post-2000). We first note that EQUATES also predicts an increase in SO<sub>2</sub> emissions from northern hemispheric Africa after 2002 (see Figure S7). However, we use EQUATES to determine if other factors such as changes in the oxidation efficiency of locally emitted SO<sub>2</sub> and meteorological changes affected our observations.”

Line 449-450: This statement seems contradictory to line 275-277 and 455.

We now more explicitly state that winter and spring time dust transport and its association with smoke explain our trends in nitrate while summertime dust transport, which does not contain co-transported smoke, is less correlated to our observed nitrate mass concentrations.

Line 469-470: This statements has not been supported by strong evidence in the paper. Figure 5 shows one month for two separate years. Comparing back trajectories for all years before and after the shift in sulfate trends would support this statement. Or the model could show transport over time as well? Are there sources of African SO<sub>2</sub> emissions that could help strengthen this statement? Does the EQUATES model show increased SO<sub>2</sub> in the emission inventories in Africa?

We now include back trajectories for the entire 21 years in the SI and state that no differences in trajectories were observed before and after 2000. We now state this in our Methods and in the Discussion. We also have added a figure in the SI showing that EQUATES also predicts an increase in anthropogenic SO<sub>2</sub> emissions from Africa.

The manuscript on Lines 563-570 now states, “As shown in Fig 6, increases in SO<sub>2</sub> in Africa, namely from anthropogenic sources, are the most probable cause for the increase in nss-sulfate levels from 2000-2011 in Barbados. Simulations from both CEDS and EQUATES reveal an increase in anthropogenic emissions of SO<sub>2</sub>. Further evidence for this speculation stems from the lack of change in air mass back trajectories before and after 2000, suggesting that emissions rather than meteorological trends are driving our observed patterns in nss-sulfate.”

Line 477: Over what time period are the highest increases in SO<sub>2</sub> occurring?

Emissions trends from Shikwambana et al 2020 indicate that increases in SO<sub>2</sub> emissions were observed starting in 1980. We now state this in the manuscript.

Line 488-489: This may be true but it has not been shown in the paper (or did back trajectories suggest this?)

We can only speculate that increased emissions of SO<sub>2</sub> in India and the Middle East may affect the nss-sulfate aerosol burden in Barbados. Back trajectories do not extend far back enough to prove or disprove this speculation.

We have made the speculative nature of this statement more apparent on Lines 590-592, "While it is possible that these two regions may also contribute to the increase in nss-sulfate observed at our measurement site, we can only speculate of their importance to the remote North Atlantic marine boundary layer."

Line 511: Again, doesn't the oxidation ratio correspond to the site location? This assumption is that the SO<sub>2</sub> is not converted before it arrives? Others have shown the importance of heterogeneous reactions with dust particles and SO<sub>2</sub> (e.g., Wang et al., 2018; Park et al., 2019), so how does that mechanism influence this argument?

We agree with the reviewer's point here. The lifetime of SO<sub>2</sub> and other oxidants is short compared to the 5 to 7-day transport time of these emissions to our site from Africa. We have now amended the text to state that our oxidation ratio calculations mainly account for the conversion of locally emitted SO<sub>2</sub> to sulfate. We now emphasize that transported sulfur is likely already in the form of sulfate due to the lifetime of SO<sub>2</sub> in the atmosphere (estimated at 20-40 hours) compared to the transport time for emissions from Africa (~5-7 days). We now specify that the oxidation ratio calculations are only to investigate the role of any locally emitted SO<sub>2</sub>, most likely from marine biogenic emissions, on the total nss-sulfate budget.

We have also observed small fractions of nss-sulfate associated in the same coarse size mode as dust and sea salt particles from size-resolved impactors. We now point out this source of nss-sulfate in an earlier portion of the manuscript where we discuss the simulated distribution of coarse and fine mode nitrate and nss-sulfate. Lines 45-450 now state, "Nss-sulfate is predicted to be almost exclusively in fine mode aerosol. While previous observations have shown that nss-sulfate dominates the fine mode in Barbados, some of the nss-sulfate is also present in the coarse mode likely due to heterogeneous reactions between SO<sub>2</sub> and coarse sea spray and mineral dust aerosols (Adams et al., 2005; Alexander et al., 2005; Li-Jones & Prospero, 1998). EQUATES does not seem to be capturing this minor yet important budget of nss-sulfate."

Reviewer #2

This study utilizes aerosol measurements from the Ragged Point site in Barbados, in conjunction with model simulations, to comprehend the effect of implementing air quality policies in the US and EU. This perspective is very interesting, given that the observation site is situated significantly distant from both the US and EU in a remote region. The implementation of air quality measures is expected to certainly influence local aerosol changes, but the effects on areas far away from the US and EU remain unclear. The long-term observational data is unique and intriguing. The data and the story have been presented clearly and meticulously. However, trace gases observation, such as NO<sub>x</sub>, SO<sub>2</sub>, and CO<sub>2</sub> are absent in these studies, making the results less robust.

The author has utilized simulated data to aid in understanding the information, which is helpful but also comes with high uncertainties. Furthermore, why is there no measurement data available after 2011? The current dataset is rather dated.

We thank the reviewer for the comments. We first point out that ion chromatography analysis of our samples stopped after 2011 and has just recently resumed with a new instrument after a new PI took over operation of the site.

I also have a concern regarding the absence of information from South America, a region geographically closer to Barbados. The local sources there may have less stringent air quality controls. In summary, addressing the following questions and comments would potentially lead to its acceptance.

We thank the reviewer for the helpful comments.

Main comments:

1) From the map, the observation site BACO is closer to South America, making its effect on BACO's aerosol more interesting to me. Do you know the ratio of wind from South America? The current study focuses on the effect of North America and Africa, which is good and interesting. However, how significant is the fraction they represent compared to the effect from South America?

We now clarify that our sector-controlled sampling is confined to 335 degrees through N and E to 130 degrees which would preclude emissions from South America. Since our sampling was active over 90% of the time, this confirms the dominant presence of easterly trade winds that would transport oceanic emissions and emissions from Africa and limited presence of emissions from South America (<10% of the winds come from this direction). We further show 21 years of air mass back trajectories in the SI which also show the dominant transport pathway is from Africa rather than South America, in agreement with our measurement site being historically used to characterize African aerosol transport.

We now state on Lines 317-320, "As has been documented in prior work (Prospero et al., 2021), the dominant transport pathways are over the ocean and traversing the African continent. Some trajectories do intercept North America and come close to Europe while few (<10%) air masses come near South America, which is outside of our sampling sector."

2) What is the aerosol and SO<sub>2</sub> lifetime compared to the travel time of air masses from North America to the site?

The lifetime of SO<sub>2</sub> is short compared to the 5 to 7-day transport time of these emissions to our site from North America. We now emphasize that transported sulfur is likely already in the form of sulfate due to the lifetime of SO<sub>2</sub> in the atmosphere (estimated at 20-40 hours) compared to the transport time for emissions from North America and other receptor sites (~5-7 days).

We now state on Lines 496-504, “We note that because the lifetime of SO<sub>2</sub> is predicted to be ~20 hours and as much as ~40 hours depending on the latitude of the source of SO<sub>2</sub> and the season (Green et al., 2019; Lee et al., 2011), our oxidation ratio estimates here are most relevant for local emissions, including sulfur emitted from marine phytoplankton (e.g., DMS). However, prior measurements at Bermuda suggest a longer lifetime for long-range transported SO<sub>2</sub> compared to local oceanic emissions from DMS, which are subject to strong condensational losses to sea spray in the marine boundary layer (Keene et al., 2014). As such, long-range transported sources from Africa, the U.S., and EU have likely been converted to sulfate upwind of Barbados and SO<sub>2</sub> concentrations shown here most likely reflect oceanic sources though some contribution from long-range transport is also possible.”

Aerosol lifetime can be much longer depending on the size, strength of deposition, and altitude of transport. Our site is a known receptor for long-range transported aerosol (on average 5-7 days of transport time) including both summertime and wintertime dust at high altitudes. We now emphasize these points in the Introduction of our paper.

3) Check all figure number in the text.

Thank you for the comment. We fixed the typos referencing figures.

4) Anthropogenic emission is one of SO<sub>2</sub> sources. However, in this study, when examining the air mass from the ocean, we cannot ignore the oceanic emission of SO<sub>2</sub> from dimethyl sulfide (DMS), which may be affected by the ocean acidification and other parameters. In the section of discussion and conclusion, the authors exclude DMS by model simulation. However, the uncertainty of DMS simulations in the model are not well refined. It would be good to find some other possible evidence to support it, e.g., recent publication about DMS vs CO<sub>2</sub>. The contribution of local SO<sub>2</sub> to aerosol and transported SO<sub>2</sub> from US and EU need to be evaluated carefully.

We now address this comment more thoroughly in the Discussion on Lines 595-609, “Marine biogenic sulfate is estimated to contribute up to 50% of nss-sulfate at Ragged Point during non-dust transport conditions (Li-Jones & Prospero, 1998; Royer et al., 2023; Savoie et al., 2002). However, our predictions of nss-sulfate and SO<sub>2</sub> concentrations with EQUATES includes DMS chemistry that does not explain our observed trends. In fact, locally emitted SO<sub>2</sub>, most likely from the ocean, is simulated to be decreasing from 2002-2011. Further, while recent studies have shown links between climate change and increased DMS emissions at high latitudes, these trends have not been demonstrated at lower latitudes. Instead, DMS is predicted to decrease with increasing temperature at low latitudes due to stratification (Kloster et al., 2007) and increasing ocean acidification (Zhao et al., 2024) while a recent modeling study, factoring in changes in phytoplankton dynamics, found that DMS emissions have not appreciably changed

from the preindustrial to the present-day (Wang et al., 2018). As such, DMS emissions do contribute to the sulfate burden but likely do not explain the recent increases in sulfate, which would also agree with findings in Bermuda where changes in the nss-sulfate burden were explained by anthropogenic rather than biogenic emissions (Keene et al., 2014).”

Detailed comments:

1) Line 18-20, 'Elevated .... in the spring of 2010 and summer and fall of.... biomass burning emissions to our site', make the sentence more clear.

e.g., 'as well as during the summer and fall of 2018', 'transported biomass burning emissions from both northern and southern Africa to our site.'

Thank you for the suggestion. We have made the proposed change.

2) Line 25: change 'predicts' to 'simulates' and apply the same for the following instances.

The change has been made

3) Line 33: add 'e.g.,' to '(NOy)'.

The change has been made.

4) Line 110: Information regarding the distance of the site from anthropogenic emissions is missing. Additionally, there is no information about the site's distance from various sources (line 245 mentioned multitude emission sources).

We now list the amount of time it takes for air masses to travel from North America, the EU, and Africa to our site in Barbados, which is approximately 5-7 days for Africa based on back trajectory analysis and longer than 7 days for transport from the EU. The site is approximately 4500 km from the west coast of northern Africa, 3000 km from the east coast of the U.S. and 6000 km from the west coast of the southern part of the EU.

5) Line 125:126: Your pump was on when the wind blows from the ocean, thereby excluding emissions from the local islands. What is the ratio of the ocean wind to the wind from south America. However, does this also exclude anthropogenic emissions from the land direction, basically South America?

We now clarify that our sector-controlled sampling is confined to 335 degrees through N and E to 130 degrees which would preclude emissions from South America. Since our sampling was active over 90% of the time, this confirms the dominant presence of easterly trade winds that would transport oceanic emissions and emissions from Africa and limited presence of emissions from South America (<10% of the winds come from this direction). We further show 21 years of air mass back trajectories in the SI which also show the dominant transport pathway is from Africa rather than South America.

We now state on Lines 317-320, “As has been documented in prior work (Prospero et al., 2021), the dominant transport pathways are over the ocean and traversing the African continent. Some trajectories do intercept North America and come close to Europe while few (<10%) air masses come near South America, which is outside of our sampling sector.”

6) Line 224-226: What does it mean? Does it imply that these two references have already presented similar results and provided explanations? If that is the case, please specify. If not, kindly make a statement regarding the changes in NO<sub>x</sub> and SO<sub>2</sub> during the same period as shown in Figure 1. The current information is unclear and difficult to comprehend.

We clarify in the Methods section that there is no measurement of gaseous NO<sub>x</sub> and SO<sub>2</sub> in Barbados. Instead, we used the EQUATES model to probe trends in locally emitted NO<sub>x</sub> and SO<sub>2</sub>.

We also clarify that the two references cited show differing responses of nitrate and sulfate to reductions in NO<sub>x</sub> and SO<sub>2</sub> in North America.

7) Fig 2: why not add the data from Bermuda.

We thank the reviewer for the comment but wish to keep the manuscript and figures focused on trends Barbados.

8) Line 233-245: The entire paragraph aims to indicate that Ragged Point is a more remote location and may be influenced by various emission sources. However, questions arise regarding the local measurements of SO<sub>2</sub> and NO<sub>x</sub>—do they exhibit similar trends to aerosols? Additionally, an inquiry is posed regarding the multitude of emission sources and how they impact aerosols in Ragged Point.

We clarify in the Methods section that there is no measurement of gaseous NO<sub>x</sub> and SO<sub>2</sub> in Barbados. Instead, we used the EQUATES model to probe trends in locally emitted NO<sub>x</sub> and SO<sub>2</sub>.

We also clarify the impact of local emissions in the Methods section on lines 137-143, “To ensure that local island emissions are not sampled, the sampling pump is only operational when the wind blows directly from the ocean (from 335 degrees through N and E to 130 degrees) with speeds greater than 1 m/s. A timer is used to record the “run time”, the total amount of time that the sampling pumps are on during the sampling interval between filter changes. Data with a run time less than 10% of the sampling interval are discarded to minimize the impact of low-speed and flukey wind conditions that might carry aerosols from local sources.”

The different emissions sources that impact Ragged Point are addressed throughout the Introduction of the manuscript. We also added a few sentences to clarify the presence of natural ocean emissions that can contribute nss-sulfate.

9) In line 125-126 you already mentioned that your pump was on when the wind direction blows from the ocean. Then how about the data from Bermuda? Add more details for Bermuda.

The site in Bermuda operates under similar sampling protocols to collect samples only when the wind is blown from the ocean.

We now mention the Bermuda sampling protocols on Lines 277-282, “The Barbados yearly concentrations differ from long-term observations of aerosol and precipitation chemistry measured at Tudor Hill, a site on the west coast of Bermuda, from 1989-1997 and from 2006-2009 as part of the same program as that at Barbados (AEROCE) and using the same protocols including sampling only when winds are over the ocean (Keene et al., 2014; Savoie, et al., 2002). At the Bermuda site, the prevailing winds come from the West so that the sampling sector extends from 180° through West to 330°.”

10) Line 246-255: Why is there no correlation between dust and sulfate, but a modest correlation between nitrates and dust? Add more details for this.

The Discussion section details the correlation between winter and spring time dust and nitrate, and we have added this information as well at the lines mentioned by the reviewer. The text on Lines 298-312 now reads, “To assess whether annual trends in nss-sulfate and nitrate observed in Barbados are associated with African aerosol transport conditions, annual average measured dust mass concentrations are also shown in Fig 2 and show no appreciable increase or decrease from 1990-2011 ( $R^2=0.06$ ). Therefore, annual trends in nss-sulfate aerosol, which show a decrease from 1990-2000 and an increase from 2000-2011, are not correlated with African dust mass concentrations ( $R^2=0.001$ ). This suggests that the increase in nss-sulfate after the year 2000 is not due to an increase in sulfate associated with heterogeneous reactions between  $\text{SO}_2(\text{g})$  and dust or to more favorable transport from Africa. Nitrate aerosol, in contrast, is modestly correlated with dust ( $R^2=0.30$ ). Comparing seasonal nitrate and dust mass concentrations by year reveals tighter correlations between nitrate and dust for DJF and MAM (0.46 and 0.4, respectively, see Fig S3). DJF and MAM are not the peak dust transport seasons to the Caribbean, but they are the seasons that favor co-transport of dust and biomass burning emissions from Sub-Saharan Africa north of the equator (Royer et al., 2023). Transport of African smoke to Barbados has been shown to be associated with elevated concentrations of nitrate, which likely explains the association between winter- and spring-time dust and nitrate (Quinn et al., 2021; Savoie & Prospero, 1982).”

11) Line 264: Seasonal trends?

The phrasing on Lines 327-330 has been altered and now reads: “Figure 3 shows trends in nss-sulfate and nitrate during different seasons (e.g., DJF, MAM, JJA, and SON). Increases in nitrate in 2008 are driven by high nitrate concentrations in JJA and SON in 2008, with most of the increase in September, while high nitrate levels in 2010 are primarily observed during MAM.”

12) Line 269-271: The days of back-trajectories for 2009 and 2010 MAM are different, does it make any difference for the analysis?

No, we are simply comparing the fraction of days in the same season (e.g., MAM) from



two years differ to illustrate the increase in transport of smoke (and dust) in 2010 compared to 2009.

13) Figure 4: Mark the year for figure 4d.

The year has been added to Figure 4d.

14) Line 308: The impact of Amazon biomass burning on aerosol levels measured at BACO can only be observed when the air mass originates from the South American continent. Current evidence in this study is not strong enough to me.

We have already addressed the lack of transport from South America at our measurement site compared to emissions from Africa.

15) Line 360-368: can be in the method.

This section has been moved to the Methods as suggested.

16) Change the order of Fig 7 and Fig 8.

The change has been made.

17) Line 412-417: can be in the method.

This section has been moved to the Methods as suggested.

18) Line 436-437: How about the agreement of nss-K<sup>+</sup> between observations and simulations?

We have added text on Lines 525-530 regarding the agreement between observations and simulations for nss-K<sup>+</sup>, "We used EQUATES data rather than our nss-K<sup>+</sup> observations, which were non-existent for most years from 2002-2011. Also, our measurements included total (i.e., fine and coarse mode) nss-K<sup>+</sup> including contributions from African dust (Savoie & Prospero, 1980). EQUATES simulations of nss-K<sup>+</sup> were a factor of 2-3 higher than our measurements except for the dust and smoke transport event that occurred in MAM of 2010."

19) Line 457-460: Compared to African wildfires, how about Amazon wildfires, which is much closer and larger.

We have already addressed the lack of transport from South America compared to emissions from Africa.

20) Line 463-466: How fast the SO<sub>2</sub> can be transported from US and EU to our observation site? Compared to SO<sub>2</sub> lifetime?

The lifetime of SO<sub>2</sub> is short compared to the 5 to 7-day transport time of these emissions to our site from the U.S. and EU. We now emphasize that transported sulfur is likely already in the form of sulfate due to the lifetime of SO<sub>2</sub> in the atmosphere (estimated at 20-40 hours) compared to the transport time for emissions from North America and other receptor sites (~5-7 days).

The text on lines 496-504 now reads, "We note that because the lifetime of SO<sub>2</sub> is predicted to be ~20 hours and as much as ~40 hours depending on the latitude of the source of SO<sub>2</sub> and the season (Green et al., 2019; Lee et al., 2011), our oxidation ratio estimates here are most relevant for local emissions, including sulfur emitted from marine phytoplankton (e.g., DMS). However, prior measurements at Bermuda suggest a longer lifetime for long-range transported SO<sub>2</sub>

compared to local oceanic emissions from DMS, which are subject to strong condensational losses to sea spray in the marine boundary layer (Keene et al., 2014). As such, long-range transported sources from Africa, the U.S., and EU have likely been converted to sulfate upwind of Barbados and SO<sub>2</sub> concentrations shown here most likely reflect oceanic sources though some contribution from long-range transport is also possible.”