Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-509-AC1, 2018

Atmospheric Chemistry and Physics
Discussions
Open Access

Interactive comment on "The impacts of regional shipping emissions on the chemical characteristics of coastal submicron aerosols near Houston, TX" *by* Benjamin C. Schulze et al.

Benjamin C. Schulze et al.

bcs4@rice.edu

Received and published: 18 September 2018

Response to reviewers:

We sincerely thank both reviewers for their helpful comments and guidance. Addressing the major points raised during the review process has substantially improved the quality of the manuscript. We have provided responses to each reviewer comment below.

Reviewer #1:

Major Comment 1:

Printer-friendly version

Discussion paper

“The meteorological resolution of 1 degree by 1 degree for back trajectories is quite coarse compared to other available datasets on HYSPLIT. With such coarse resolution, the question arises as to how well that dataset captures the land-sea interface and related meteorological dynamics (e.g., diurnal land-sea breezes, continental air mass outflow and recirculation back to the coast). Given that your monitoring site is right on the coast, this could be a significant issue. Some comparisons that would help allay such concerns would be (a) to compare wind roses generated with observed data and wind roses generated with the GDAS 1x1 dataset at the observation lat-lon and for each of the defined meteorological regimes and (b) compare back trajectories from the 1x1 dataset with a sample of those generated from the available 3 km resolution data (HRRR, more than an order of magnitude higher resolution). For (b), do the 3 km back trajectories identify any continental recirculation, especially for the defined ‘marine’ periods?”

Response:

This is a very valid point. To address this issue, we have re-calculated all backward trajectories using 12 km x 12 km data from the North American Mesoscale Forecast System (NAMS) archive (obtained through HYSPLIT program). The domain of the 3-km data mentioned by the reviewer does not encompass all of the Gulf of Mexico, according to the HYSPLIT website (see https://ready.arl.noaa.gov/archives.php, HRRR 3km, Grid domain map), and was therefore not used. This modification has caused Figures 2, 5, 8 and SI Figures S11, S16, S17, and S20 to be updated.

We further note that our distinction of the “continental” period as in fact continental was based on a combined analysis of local wind directions, back trajectories, trace gas concentrations, and submicron aerosol characteristics. Due to the numerous indicators of continental influence, we are confident in our classification of the four day period as such. As for any continental influence during periods previously classified as “marine,” back trajectories calculated using the NAMS data confirm that the marine period was free of any recent continental influence due to recirculation.

Major Comment 2:

"The Savoie et al. paper reports Bermuda and Barbados marine nss-SO4/MSA mass ratios as 19.6 ± 2.1 and 18.8 ± 2.2 (as listed in that paper's abstract). So the corresponding marine MSA/nss-SO4 ratios are 0.051 and 0.053 for Bermuda using the Bermuda ratio. Bermuda does match up better with your monitor latitude, so you likely need to recalculate using the 0.051 ratio."

Response:

This is an astute observation by the reviewer. However, we have concluded that the authors of Savoie et al. (2002) accidentally switched the ratios for the islands when composing the abstract. Within the main text, the authors report the equation describing the prediction of nss-SO4 at Bermuda as:

Bermuda: Nss-SO4 = 18.8(±2.2)MSA + 28,600(±1200)Sb.

And for Barbados as:

Barbados: Nss-SO4 = 19.6(±2.1)MSA + 18,000(±1200)Sb.

As these equations represent the true results, we have already applied the Bermuda ratio to our analysis (1/18.8 = 0.053).

Major Comment 3:

"Figure 5 (and all maps depicting the ECA region). The ECA region drawn on Figure 5 and other maps is substantially incorrect. The ECA is not in effect in the territorial waters of other countries. Hence, the ECA is cut off at the US-Mexico border and, more significantly for this analysis, narrows substantially around Florida's southern and south-eastern region due to the territorial waters of Cuba and the Bahamas. For a full description of the ECA boundaries, see https://www.epa.gov/sites/production/files/2016-09/documents/mepc1-circre-na-eca.pdf. ECA boundary shapefiles for mapping purposes are readily available on the web.”

Response:

This is another great point. We were not originally aware that shapefiles existed, and as such we had simply created a boundary extending 200 nautical miles from the coast of the U.S. All relevant figures have been updated to include the true ECA region.

Major Comment 4:

“A Gulf marine anthropogenic emissions source that needs to be considered and discussed in this paper is emissions from offshore oil and gas platforms (e.g., gas flaring, support operations). While the WPSCF analyses presented in Figure 5 suggests less contribution from areas where these sources are located, compared to contributions in the shipping lanes, the authors should perform a similar emissions analysis for these sources as was done for point sources in Florida (i.e., historical and current SOx emissions comparisons).”

Response:

We thank the reviewer for this insightful comment. We have added the following paragraph to Section 3.3 (lines 495-507).

“Offshore oil and gas extraction operations represent another source of SO2 emissions within the Gulf of Mexico. Under the Clean Air Act, regulation of currently operating offshore oil and gas sites is handled by the Department of the Interior’s Bureau of Ocean Energy Management (BOEM). As can be seen from Figure 5, all currently operating sites are located within the NA-ECA (Wilson et al., 2017). According to the BOEM 2014 Gulfwide Emission Inventory Study, annual SO2 emissions from platform and non-platform oil and gas operations totaled 7,150 tons (Wilson et al., 2017). Within the same study region, SO2 emissions from commercial marine vessels were estimated at 48,215 tons (Wilson et al., 2017). The discrepancy between marine vessel SO2 emissions reported in the BOEM inventory (48,215 tons) and that of Johannsson et al.

(2017) (75,000 tons) for the Gulf of Mexico is due to the limited spatial scope of the BOEM study (only the Western Gulf of Mexico was considered). While non-negligible, offshore operations therefore represent less than ~15% of SO2 emissions in the western Gulf of Mexico and less than ~10% of total SO2 emissions in the entire Gulf of Mexico."

Ultimately, as offshore oil and gas platforms represent such small fraction of total SO2 emissions within the Gulf, we conclude that our major findings regarding the influences of marine vessel emissions are not substantially influenced or called into question. However, we have also added the locations of currently operating O&G platforms to Figure 5 in response to this comment and a similar comment from Reviewer #2.

Major Comment 5:

"Assuming ECA compliance, it is not at all clear that there will be significant NOx reductions when switching to lower sulfur fuels. Browning et al. (2012) reports only a very small benefit, 1-6% reductions in NOx, due to fuel switching. The paper would benefit from the authors exploring this lack of significant NOx benefit in the ECA regulations, and its implications on the perturbations caused by marine shipping before the ECA and after. The ECA does include some NOx regulations that went into effect in 2016 (Tier III engine standards), but the immediate benefit of this is unclear."

Response:

We agree with the reviewer that fuel switching may not lead to reductions in NOx emissions. The Tier III standards are likely to have a delayed effect over time (rather than an immediate effect) as engines/ships are replaced. Ultimately, we conclude that the reason for the enhanced level of atmospheric processing observed in the "shipping influenced" period relative to the "marine-biogenic" period in Section 3.4 is due to alignment with shipping tracks rather than simply transit outside vs. inside the ECA. However, we note that this point was not clear in the original manuscript. Our revisions to this section are included in the following bulleted list:

1: Original sentence (now lines 584-586):

Assuming ECA compliance, these air masses should receive only a small fraction of the particulate, SO2, and NOx emissions encountered by those originating outside the boundary (Lack et al., 2009; Lack et al., 2011; Browning et al., 2012).

Author edits:

The claim that air masses encounter fewer NOx emissions within the ECA has been removed.

2: Added sentence on page 29, lines (654-657)

Added sentence:

“Based on this information, it appears that air mass transit within major shipping corridors is associated with more processed organic aerosol relative to background marine conditions in the Gulf of Mexico.”

3: Added paragraph to the end of section 3.4 on page 30, lines (673-683)

Added paragraph:

“However, it should be noted that unlike SO2 emissions/concentrations, the presence of the ECA may not substantially reduce concentrations of atmospheric oxidants within shipping plumes. Numerous studies have linked shipping-related perturbations of marine OH radical concentrations to vessel NOx emissions (e.g., Lawrence and Crutzen, 1999; Kim et al., 2013). While Tier III NOx emissions standards implemented in the ECA in 2016 are projected to slowly reduce emissions over time (as standards only apply to vessels constructed in 2016 and later), Browning et al. (2012) have shown that the sole switching from high sulfur HFO to MGO at the ECA border in the Gulf of Mexico only produced NOx reductions of 1-6%. As a result, the effect of shipping emissions on marine OA processing likely depends more on whether air masses align with shipping lanes during transit than whether such transit occurs within or outside of the current ECA.”

Major Comment 6:

“There is a large body of research that has been done on ship emissions and their impact on marine aerosol optical properties, including ALW. As one example, see publications related to the Monterey Area Ship Tracks Experiment. So I think it is likely that there is significant information available related to “measurement-based predictions of the role of shipping on the production of ALW in coastal marine environments.” Have the authors delved into this body of literature?”

Response:

We thank the reviewer for bringing this point to our attention. We think that this can be addressed by including a better explanation of how our study differs from past shipping-emissions related studies with respect to aerosol liquid water. To clarify, we are not claiming that there is a lack of research on the impacts of shipping emissions on clouds (and the liquid water associated with marine clouds) but rather that there has been little research on the non-cloud related impacts of aerosol liquid water associated with shipping-influenced marine particles. As a growing body of recent literature has shown, ALW can substantially impact organic aerosol formation mechanisms (e.g., Carlton and Turpin, 2013; Li et al., 2015; McNeill et al., 2015). However, we have yet to see any research investigating the extent to which ALW associated with shipping related particles can influence organic aerosol formation. We have edited the first paragraph in Section 3.6 as follows:

Original:

“Despite the fact that shipping emissions produce substantial amounts of hygroscopic SO4 aerosol, there have been few measurement-based predictions of the role of shipping on the production of ALW in coastal marine environments. In addition, organic gases capable of partitioning to ALW are present throughout the MBL (Sinreich et al., 2010), have elevated concentrations near the coasts (Fu et al., 2008; Fu et al., 2011), and contribute significantly to aerosol mass in both rural and urban areas within the southeastern United States (Li et al., 2015). As a result, measurement-based modeling of ALW is needed to inform understanding how future changes to shipping sulfur emissions may influence SOA formation in coastal environments. “

Edited Version (now page 33/34, lines 735-750):

“While the impacts of shipping emissions on marine cloud condensation nuclei concentrations, cloud formation processes (e.g., ship tracks) and cloud properties (e.g., increased albedo, increased droplet acidity) have been extensively studied in the recent past (e.g., Coakley et al., 1987; Durkee et al., 2000; Coggon et al., 2012; Peters et al., 2012; Sorooshian et al., 2015b), there have been few measurement-based analyses of the role of these emissions on the production of ALW and subsequent OA processing in coastal marine environments. The injection of SO2 and production of SO4 aerosol mass in the marine boundary layer, combined with high ambient relative humidity levels, will lead to a substantial mass concentration of ALW associated with submicron anthropogenic particles, even in cloud-free conditions. As organic gases capable of partitioning to ALW are present throughout the MBL (Sinreich et al., 2010), have elevated concentrations near the coasts (Fu et al., 2008; Fu et al., 2011), and contribute significantly to aerosol mass in both rural and urban areas within the southeastern United States (Li et al., 2015), the production of this partitioning medium over the marine boundary layer may impact SOA production. As a result, measurement-based modeling of ALW is needed to inform understanding of how future changes to shipping sulfur emissions might influence SOA formation in coastal environments.”

Minor Comments:

Comment 1 (original line 87):

The Kotchenruther (2016) paper showed only 2 sites (not 3) along the gulf coast that had significantly less average reductions compared to the other sites analyzed.

Printer-friendly version

Discussion paper

Response:

This has been changed to 2.

Comment 2 (original line 175):

The html link is broken, replace with working link.

Response:

Replaced

Comment 3 (original lines 333-334):

In addition to the hypothesis of a major anthropogenic source in the gulf, recirculation of continental air masses could also support the observed elevated SO4.

Response:

We agree that this would be a possibility, but back trajectory analysis, combined with the consistent observation of elevated sulfate levels, suggests recirculation is not the primary mechanism producing elevated sulfate. We have edited the sentence as follows:

Original:

"The observation of SO4 mass loadings much larger than 1 μg m-3, which is generally the maximum observed in remote marine locations, even during periods of high biological activity (Zorn et al., 2008; Rinaldi et al., 2010; Schmale et al., 2013; Ovadnevaite et al., 2014), supports a major anthropogenic aerosol source in the Gulf of Mexico."

Edited: Now page 16, lines 335-341

"The observation of SO4 mass loadings much larger than 1 μg m-3, which is generally the maximum observed in remote marine locations, even during periods of high biological activity (Zorn et al., 2008; Rinaldi et al., 2010; Schmale et al., 2013; Ovadnevaite et al., 2014), supports either a major anthropogenic aerosol source in the Gulf of Mexico or an influence from continental recirculation; however, backward trajectory analysis combined with an investigation of relevant source magnitudes, described in Section 3.3, points to a marine anthropogenic source."

Comment 4 (original lines 377-378):

How well do diurnal profiles match the land/sea breeze pattern? Could this simply represent the difference between continental and marine air?

Response:

During the continental period, mass loadings of the OOA-2 factor tend to increase around 8-9 AM local time. While this does coincide with shifting wind directions, winds shift from primarily offshore flow at night to onshore flow during the day. As there is no evidence of an offshore organic aerosol source capable of producing the magnitude of OOA-2 mass loadings observed midday (~7-10 μg m-3), this suggests that either recirculated VOCs are being rapidly oxidized, or that an organic aerosol layer that resided in the free troposphere at night (and was therefore transported out to sea at night above the marine boundary layer) is mixed downward with expansion of the boundary layer in the morning. We recognize that the second possibility was not mentioned in the sentence referenced by the reviewer, so we have edited the sentence as follows:

Original:

"Diurnal profiles of NR-PM1 species highlight the influence of local photochemistry on aerosol formation (Figure 3)."

Edited: Now page 18, lines 386-389

"Diurnal profiles of NR-PM1 species highlight the influence of local photochemistry and/or boundary layer dynamics (i.e., downward mixing of aged OA into the growing boundary layer) on aerosol mass loadings (Figure 3)."

This has also caused us to modify the next sentence as follows:

Original:

“OOA-2, the dominant PMF factor during this period (72%), displays a photochemical dependence similar to previously extracted OOA factors in Houston’s urban core (Cleveland et al., 2012) but is much more oxidized (O:C = 0.79 in this study versus 0.46 in Cleveland et al. (2012)), highlighting the effect of aging during transport.”

Edited: Now page 18, lines 389-392

“OOA-2, the dominant PMF factor during this period (72%), displays a diurnal profile similar to a previously extracted OOA factor in Houston’s urban core (Cleveland et al., 2012) but is much more oxidized (O:C = 0.79 in this study versus 0.46 in Cleveland et al. (2012)), highlighting the effect of aging during transport.”

We have changed “photochemical dependence” to “diurnal profile” due to the uncertainty regarding the specific mechanism leading to rapid production of OOA-2 in the morning during the continental period.

Comment 5 (original lines 559-560 and Figure S20):

Once the ECA boundaries are properly drawn on the maps presented (see comment related to Figure 5), the authors should also point to the significant narrowing of the ECA boundaries off the SW, S, and SE coast of Florida as a potential source of unregulated ship emissions.

Response:

The following line has been added to the captions of Figures 5, 8, S11, S16, and S20.

“Note that the ECA boundary is narrowed on the southeastern coast of Florida due to proximity to the territorial waters of Cuba and the Bahamas.”

Comment 6 (original lines 559-560 and Figure S20):

As mentioned in another comment, the ECA boundary is significantly incorrect as

Printer-friendly version

Discussion paper

drawn and is not in effect in Mexican territorial waters. So there is a much larger portion of the back trajectories mentioned here that are outside of the ECA regulation zone. Having said that, the trajectories are not in major shipping lanes, so the authors' line of reasoning is still supported.

Response:

After updating the backward trajectories using 12km x 12km data, the “marine-biogenic” period trajectories were somewhat altered. However, our conclusion that they likely represent marine conditions unaffected by shipping emissions is still supported. We believe no edits are necessary in response to this specific comment.

Comment 7 (original lines 812-817):

Can the authors reach any conclusions about the relative dependence of marine OOA-3 production on anthropogenic nss-SO4 emissions vs. anthropogenic NOx? If global shipping FSC lead to further SOx decreases in 2020, but there are only relatively modest NOx reductions, how would that effect marine OOA-3 production (i.e., do you still expect significant reductions, or less of an effect)?

Response:

While we consider this to be an interesting question, we do not think that the data collected provide enough information to try and address it. While we presume that OOA-3 production is more likely associated with SO2 emissions than NOx emissions (due to either co-emission of large MW VOCs during HFO burning or enhanced partitioning of semi-volatile or intermediate-volatility species due to increased ambient aerosol mass from SO4), we are hesitant to make that conclusion within the paper to avoid over-interpreting the data.

Reviewer #2:

Major Comment 1:

“The shipping routes in and out of Houston overlap with the significant offshore oil extraction occurring all along the coastline. It is surprising that the potential for emissions from oil and gas extraction activities are not discussed, especially given the result that total PM produced from offshore sources was similar before and after adoption of the low-sulfur fuel regulations. Some analysis and discussion of oil and gas production as a possible sources is warranted in the paper. Also, please add a plot of offshore drilling activities to Fig 5.”

Response:

This is a valid point that was also brought up by Reviewer #1. Please see response to Major Comment 4 from Reviewer #1. We have added the O&G sources to Figure 5.

Major Comment 2:

“Sea-salt sulfate is estimated in proportion to sea-salt chloride which is semi-volatile and may be replaced by nitrate. It would be more accurate to use sodium for this analysis, or make the argument that combined chloride + nitrate totals are low and so sea-salt sulfate must also be low. This argument should be presented at the first point where sea-salt sulfate is first quantified.”

Response:

We thank the reviewer for highlighting this fact. Submicron sodium measurements were not available during the campaign, however, as the reviewer astutely points out, it is unlikely that a significant mass of sea salt chloride is “missed” due to chloride displacement, as average nitrate mass loadings were only $\sim$0.02 μg m-3 during the marine period. We have added a sentence to the end of the description of sea-salt sulfate quantification (now lines 295-298) explaining (and refuting) this possibility.

Major Comment 3:

“The measurement period of three weeks seems relatively short when attempting to draw general conclusions about the concentration and nature of the marine aerosol.

The trends in Fig 2 and Fig 4 illustrate variations at multiple time scales including some that may be longer than the three week measurement period. The authors should note the limitations inherent in the three week measurement period when attempting to draw general conclusions."

Response:

While we agree with the reviewer that a three-week campaign is not long enough to draw definitive conclusions about the nature of marine aerosol, field campaigns around the world frequently utilize this general timeframe due to logistical constraints. We have added the following statements at the following locations within the manuscript to highlight the limitations of this timeframe:

1: Addition to Section 2.1 (lines 125-128):

"As measurements were performed during a single three-week period, presented results should be viewed with this limitation in mind. Ultimately, longer time-frame studies are warranted to test whether results presented here are consistently observed."

2. Addition to Section 3.1 (lines 351-352):

"However, as these comparisons are based on only three to four weeks of summertime data collected before and after implementation of the regulations, the results should be interpreted with this limitation in mind."

3. Addition to Section 3.3 (lines 577-578)

"However, longer term observational or modeling studies are nevertheless needed to more definitively quantify the effect of the ECA."

2. Addition to Conclusions (lines 864-865)

However, longer term studies are warranted to fully investigate this possibility.

Major Comment 4:

"The comparison of the mechanistic WSOC predictions in Houston to the results from a different box model calculation carried out in Los Angeles seems inappropriate. The humidity, mix of sources, and atmospheric chemical regimes in Los Angeles make this a poor comparison point for Houston. The authors reference several modeling studies carried out specifically for Houston. These should provide a better comparison point to judge if the amount of aqueous SOA associated with marine aerosols/shipping emissions is reasonable."

Response:

We disagree with the reviewer's comment that mentioning the Los Angeles study is inappropriate. The Los Angeles study is mentioned in order to highlight a possible anthropogenic SOA production pathway not included in our modeling method (due to lack of appropriate measurements in Houston), but possibly relevant as shown in other major urban cities. We do not "compare" our results to those from LA in any quantitative sense, as the reviewer's comment seems to suggest, and we do not use the Los Angeles results to demonstrate that our results are reasonable. Rather, we note the specific magnitude of this pathway in Los Angeles to demonstrate to the reader that the P-S/IVOC SOA production pathway is potentially substantial in urban locations. Furthermore, the P-S/IVOC SOA production pathway presented in the Los Angeles study is mentioned solely to emphasize why our result regarding the significance of aqSOA may be an overestimate. Not mentioning this potential pathway would therefore represent a deliberate attempt to lead the reader to over-interpret the significance of our conclusions. However, we then compare our results to Houston measurements to obtain an estimate of the contribution of the AMA aqSOA production mechanism relative to measured ambient OA mass loadings.

In terms of a comparison of our modeling results with those from the Houston study by Li et al. (2015), as the reviewer suggests, we have changed the following sentence in lines 839-843 from:

“Still, the AMA effect is responsible for 0.2-0.35 μg m3 of ambient aqSOA according to the model calculations, which represents 4-6% of ambient OA measured by Cleveland et al. (2012) near downtown and ∼10-17% of average OA measured in Houston’s urban core by Leong et al. (2017)”

To:

“Still, the AMA effect is responsible for 0.2-0.35 μg m3 of ambient aqSOA according to the model calculations, which represents 4-6% of ambient OA measured by Cleveland et al. (2012) near downtown, ∼3-5% of OA modeled using CMAQ by Li et al. (2015), and as high as ∼10-17% of average OA measured in Houston’s urban core by Leong et al. (2017).”

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-509, 2018.

Printer-friendly version

Discussion paper