

Comments on “Aircraft measurements of aerosol and trace gas chemistry in the Eastern North Atlantic” by Zawadowicz et al.

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December 10, 2020

ACP criteria

Does the paper address relevant scientific questions within the scope of ACP?

Yes

Does the paper present novel concepts, ideas, tools, or data? Yes, primarily the data.

Are substantial conclusions reached? This is weak, as discussed below. There’s little in the way of new conclusions.

Are the scientific methods and assumptions valid and clearly outlined? Pretty much.

Are the results sufficient to support the interpretations and conclusions? Yes.

Is the description of experiments and calculations sufficiently complete and precise to allow the results to be reproduced? yes, insofar as it’s possible to reproduce an experiment where the weather matters.

Do the authors give proper credit to related work and clearly indicate their own new/original contributions? Yes.

Does the title clearly reflect the contents of the paper? Yes.

Does the abstract provide a concise and complete summary? Yes.

Is the overall presentation well structured and clear? Pretty good.

Is the language fluent and precise? Generally yes.

Are mathematical formulae, symbols, abbreviations, and units correctly defined and used? Generally yes, though formulae are not formatted according to Copernicus rules.

Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined,
Some of the plots aren't really easy to read.

Are the number and quality of references appropriate? That's discussed below.

Is the amount and quality of supplementary material appropriate? Yes.

Overall comments

This paper was a bit frustrating to read. The experimental work seems to have been done well, and it appears to be a valuable dataset for future work, but there are three fundamental issues that are given short shrift here and really ought to be improved before the paper is accepted: the literature review is woefully inadequate; the meteorological context is largely omitted, and much more could have been done with the discussion.

Literature review

The authors seem to have spent very little effort seeking prior data about aerosol chemistry projects near their study area, even though Azores and surrounding ocean have been a pretty common site for field projects. They did not have the time resolution, CIMS or CCN, but the sulfur chemistry in the central North Atlantic has been studied at least as far back as 1987 (Galloway, Penner, et al. 1992; Galloway, Keene, et al. 1990; Pszenny et al. 1990) and the ASTEX/MAGE project, employing aircraft, ground stations, and a ship, was based in the Azores in 1992 (Blomquist, Bandy, and Thornton 1996; Huebert et al. 1996; Zhuang and Huebert 1996). I was really puzzled that no mention was made of them. The ACE-2 project (Quinn et al. 2000; Raes et al. 2000) was centered a bit farther south, but seems relevant, as do some oceanographic cruises (e.g. Andreae et al. 2003).

The authors apparently made the rather peculiar decision that only other projects featuring AMS measurements were worth considering, resulting in rather tenuously related comparisons (the Amazon basin, and biomass burning plumes from Southern Africa, for example.) Even then, there are more appropriate comparisons than the ones used. VOCALS looked at another clean cloud deck (Shank et al. 2012; Wood et al. 2011). ATOM passed through your study area 4 times with a huge payload, including AMS and CIMS (Wofsy et al. 2018).

I cannot fathom why there is no mention of any of the many studies based at Mace Head, on the west coast of Ireland (e.g. Dall'Osto et al. 2010; Ovadnevaite et al. 2014).

Meteorological context

The meteorological setting is woefully incomplete. What was typical cloud height? Was there usually an extensive stratocumulus deck? What altitude? Was the boundary layer decoupled? Was there a strong inversion? Was there a buffer layer? Was there drizzle that

might be scavenging aerosol? Why were the altitude ranges 0 m to 1000 m and 1000 m to 3000 m chosen? I presume it had to do with boundary layer depth, but that should be explicit. Using fixed altitude ranges is convenient, but does it really reflect the structure of the atmosphere? It is often best to group data into mixed layer, cloud layer, buffer layer (if present), and free troposphere.

Are there estimates of entrainment velocity during the experiment? That would constrain how fast the MBL is diluted with FT air and thus give a lower bound on MBL sources of aerosol. Or was the meteorological situation too complex for such approximations to make sense?

Discussion

Since the literature survey was so minimal, I suppose it was inevitable that there would be a lack of direct comparison with earlier data from the region. But it would be interesting to know whether things have changed. Of particular interest is the fact that earlier experiments found much more MS^- . Is that a real change, or is it possibly that much of the MS^- was on particles too large for the AMS? Were the $MS^-:DMS$ or $MS^-:SO_4^{2-}$ ratios different? Is the aerosol sufficiently acidic to drive off HNO_3 ? (I strongly suspect that's why you saw so little NO_3^- ; it was displaced to seasalt particles too big for the AMS to detect.)

I was also a bit surprised to see no estimates of how much of the aerosol in the boundary layer could have come from the free troposphere. Without level legs at the top of the MBL, you obviously cannot do a flux study, but you have tracers of long-distance transport that are immune to precipitation scavenging (CO, benzene, toluene) and at least 1 that is not (BC). Can you use those to put some bounds on how much of the SO_4^{2-} and organic aerosol came from above? Would that bring the $MS^-:SO_4^{2-}$ in line with other work?

The dramatic split in Fig. 6b in pH_F is interesting. Since Table S1 says there were 5 profiles on 19 July, it seems likely that some profiles were in the putative fire plume while others were not. It might be worth trying multiple back trajectories on each of the profiles to establish a pattern like that seen in Clarke et al. (2013), where the ensemble of trajectories and their correlation with aerosol properties lent credibility to the trajectories over rather long distances.

Those early experiments had far less data, but did more with it, examining budgets and processes, not just using back trajectories to conclude that sometimes continental aerosol was present and sometimes it was really clean. You have more, better quality data, and it's integrated with a larger instrument package, so you ought to be able to do more.

More specific comments

line 21 “fully” is meaningless. It suggests that all possibly relevant instrumentation was aboard, and that's not possible even on much bigger aircraft.

- line 26** average submicrometer non-refractory aerosol mass
- line 33** “1 % of the sulfate and no more than 3 % of the total aerosol” makes no sense. You presumably meant no more than 3 % of the submicron organic aerosol.
- line 140** Was there a typical altitude range of the spirals? “Through the atmosphere” is vague (and strictly speaking, incorrect). Was there a minimum altitude span criterion for inclusion in Table S1? Were there any criteria for where to do the spirals?
- line 145** Was the standard aerodynamic lens used? What temperature was the vaporizer?
- line 155** Has the inlet efficiency for this inlet been characterized?
- line 156** “switched ... based on cloud cover” seems unlikely. Surely switching was done based on whether the plane was actually in cloud.
- lines 166–167** I’m a bit surprised at all the English (rather than SI) units. I guess that’s up to the journal editors. In addition, the OD of the tubing is irrelevant; it’s the ID that matters.
- line 186** The low supersaturation is presented inconsistently. Here and in Fig. S3 it is 0.1 %, while in Fig. 13 it is 0.13 %.
- line 173** I don’t see how elevated DMS background in the summer IOP necessarily biases DMS measurements high. If it is indeed an isobaric interference (any idea what would do that?) then one would eliminate the overestimate by subtracting the background. If it was incomplete destruction of the DMS, then subtracting the background would produce an underestimate. If the interfering species was partly destroyed by the catalyst, then yes you would have an overestimate of DMS, but you could only claim that the patterns you see in DMS are accurate if the interfering species concentration was fairly constant.
- line 182** “more closely mimic” is incomplete. More closely than what?
- line 229–230** Has anyone ever claimed that MSA accounted for the majority of particulate sulfate mass?
- line 235** The equation is only true if those species are the only acids and bases present in the aerosol. There are organic acids like oxalic acid and MSA. They are probably negligible here, but that ought to be noted.
- lines 242–245** Be more explicit about the use of the thermal denuder. Was there very little submicron seasalt (as is likely)? As determined by heating to what temperature? It’s true that the AMS doesn’t see coarse particles, so whether they are externally mixed seems irrelevant. Is there a claim here that there was little volatile material on coarse particles so the AMS wasn’t actually missing significant MS^- and NO_3^- ?

line 250 It's not wrong, but a bit odd to use a moving average with an even number of points, meaning that the time represented by the average is between the times of two data points, but not right on them. I suppose it doesn't matter here since there aren't any comparisons here that depend on close synchronization.

line 275 Acid-catalyzed reactive uptake of organic vapors is an interesting idea. Any citations for it? Could SOA production via that mechanism be fast enough to account for the extra organic aerosol in the MBL?

line 371 (This is a hobbyhorse of mine.) Airmasses do not have origins! The air always came from somewhere earlier and has traces of that left in it. If there was near-total scavenging event or a large influx of pollution that dwarfs whatever was present, then one could claim there is an origin of the characteristics of the air mass. Ascribing an origin to an air parcel in the MBL is particularly absurd, since there is almost always entrainment mixing going on meaning that much of the air was in the FT within the last few days. Simple back trajectories are not really capable of conveying that.

line 402 Surely you men "summer and winter" rather than "summer and fall".

Fig. 4 It's jarring that the pie charts for the organic fraction of the aerosol are larger than the the total aerosol.

Fig. 6 This is an interesting figure, but the caption isn't as clear as it ought to be. It appears that in panels A and B, the organic loading is averaged into 100 m bins, while the pH_F is for individual (10 s?) averages. The pH_F data in panel B has a remarkable split between nearly neutralized and very acidic aerosol, as though some of the 5 spirals that day were in the pollution plume while the others were not. Of course the averaged organic loading cannot show that. Would it be worth plotting the spirals separately, or grouped as plume vs. non-plume? Were panels C, D, and E for the entire vertical profile? What does "normalized" mean here? Same area under the curve? It didn't happen often, but it appears from panel C that MS^- was sometimes 10% to 15% of the SO_4^{2-} . Is that real?

Fig. 14 While the maps are quite pretty, there is a lot of information, such as bathymetry, that is unimportant to the paper. I don't actually object much to that even though it is best practice to exclude irrelevant material from graphics. However, including the political divisions within countries is clearly excessive.

Equations in the supplement I assume the Copernicus editors will help you figure out what should be italicized and what should not be.

CE of MSA in the supplement This is a misinterpretation of Middlebrook et al. (2012). It's not the pH that matters—it's whether the aerosol is liquid or solid. That said, since MSA salts are solid and MSA itself is liquid (much like H_2SO_4 and salts thereof),

the CEs you propose are reasonable in the lab. I'm not sure what you're doing with the field data—the particles are presumably internal mixtures with only small contributions from MS^- . In that case, it's the presence of liquid H_2SO_4 that will determine CE for the entire aerosol.

PIKA vs Squirrel Did you get $I_{\text{CH}_3\text{SO}_2^+}$, $I_{\text{CH}_2\text{SO}_2^+}$ and $I_{\text{CH}_4\text{SO}_3^+}$ from PIKA or did you use unit mass data from Squirrel? I guess you did it with PIKA, which would make sense, particularly in the field, where other species would be present at those unit masses. To look for interferences, it might be useful to plot $I_{\text{CH}_4\text{SO}_3^+}$ vs $I_{\text{CH}_3\text{SO}_2^+}$ and $I_{\text{CH}_2\text{SO}_2^+}$ vs $I_{\text{CH}_4\text{SO}_3^+}$ to see whether you have the same fragmentation pattern in the field as you had in the lab.

Table S1 Including 4 digits after the decimal point for latitude and longitude specifies the point to within 11 m. Seems excessive. Might be useful to add an altitude range, unless that was constant (in which case I'd like to see that somewhere).

Fig. S3 The y axes on panels E and F are labeled SO_4 rather than NH_4 .

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