Response to Anonymous Referee #2

Summary and Overall Recommendation:
This study examines the contribution of nitrated aromatic compounds (NACs) to light absorption of aqueous particle extracts and particulate brown carbon (BrC) from samples collected mainly from Germany and some from China. Aerosol samples were collected onto quartz fiber filters using high-volume filter samplers. The authors focus on 8 NACs, which included nitrophenols and nitrated salicylic acids), previously recognized from prior lab and field studies to contribute to BrC. The novelty in this study lies in the fact that the authors compare the contributions of NACs to WSOC mass and aqueous aerosol extract light absorption from 4 locations in Germany and 2 locations China. Mainly summer versus winter comparisons are made in Germany and only summer data are obtained from China. The spatial comparisons are quite interesting as the authors know when some of these sites are directly affected by biomass burning (BB events). Overall, this study will be of interest to many readers of ACP; however, there are a lot of technical issues that need to be addressed (as outlined below) before publication can be fully considered. In addition, it would have been more interesting if the authors would have gone further in the chemical characterization of the BrC components collected from these different locations and seasons, especially considering that the NACs didn't explain a larger fraction of the BrC mass. As the authors indicate in the last lines of their paper within the conclusions section, the exciting new results lie in identifying new tracers for BrC that indicate source and chemical process. With that said, I do think many researchers working in BrC aerosol will find this paper interesting due to the use of known BrC constituents (NACs) and comparing their trends between locations and seasons to gain insights into their potential sources. The comparison of the German winter sites to the Chinese summer sites isn't surprising, but it is compelling to see that BB likely contributed to the NACs concentrations at the German winter sites where as other sources (one I mention below in the specific comments section) contribute to NACs levels in China during summer.

We would like to thank the referee for the recommendation and the helpful suggestions. We agree, that it is indeed interesting to characterize BrC components further. Therefore, we are going to consider also other possible BrC compounds in forthcoming studies. Nevertheless, the focus of this study was to characterize NACs as BrC components.

Specific Comments:
1. Important details missing for the high-volume filter sampling protocols: How were the quartz fiber filters treated before sampling? Were they pre-combusted before sampling, and if so, at what temperatures and for how long? How were these filters stored after collection? Were they stored in pre-combusted Al foil packets or some other kind of container? How long were filters stored before chemical analyses and how did this affect the data presented here? Did the authors determine the recovery efficiencies of NACs from this filter media and was this considered into the calculations for their mass concentrations? The authors stated that the samples were stored at -20 °C. Please clarify that this was under dark conditions too of course. Even though it may seem trivial, these details really should be added to the experimental section.

Details on the high-volume filter sampling protocol were added to Section 2.2 as suggested by the referee.
The paragraph reads now like this (p. 4, l. 37 – 40):
"PM_{10} was collected on quartz fiber filters with a Digitel DHA-80 high volume filter sampler (MK 360, Munktell, Falun, Sweden, flow rate: 0.5 m3 min-1). To minimize blank content, the filters were pre-baked for 24 h at 105 °C. Day and night samples (11 h or 12 h, see Table 1)

were taken during each campaign except for Melpitz (winter) and Melpitz (summer), where particles were collected for 24 h. After sampling, filters were stored in clean aluminium tins at -20 °C in the dark until extraction (extraction was done within a year after sampling). It is assumed, that storage at -20 °C prevents chemical degradation of the sample."

Regarding the question about recovery efficiencies from filter media:
An accurate determination of recovery efficiencies from filter media is not easily possible. One might spike a blank filter with a standard solution to determine recoveries from the filter. However, since the target compounds are actually part of an aerosol particle and extracted from aerosol particles and not the filter media, this method is not accurate. The investigated NAC compounds in our study are water soluble. Hence, due to the relatively large amount of water used in the extraction process and the water solubility of NACs, it is expected that NACs dissolve completely into water.

Referring to recovery efficiencies of the used enrichment method: Matrix effects and recovery efficiencies in the HF-LPME method are considered in the calculation of nitrophenol mass concentration according to the published method in Teich et al. 2014.

2. Extraction solvent:
Can the authors comment on how well water extractions remove BrC constituents from the filters? Why wasn't another solvent, such as an organic solvent, considered as well in this study? I ask this question since HULIS-like species, which are likely oligomeric in nature, may not have been well removed from the filter media. As the authors know, HULIS-like species can contribute to the BrC fraction. Lin et al. (2014, ES&T) found that the BrC fraction within IEPOX-derived SOA was highly oligomeric in nature but also less water soluble, so extracting the filters with an organic solvent was really important in discovering these light-absorbing oligomers. This tudy isn't the only one to consider this issue, but certainly a recent example to consider in terms of extraction solvent.

We agree, that methanol or other organic solvents may remove BrC constituents with a higher efficiency from filters than water. However, the solvent of choice is also dependent on the target compounds and the overall aims of the study. In our case, the focus of our study was on NACs. NACs are expected to be fully soluble in water. Considering that water is also a natural solvent in the atmosphere, we believe that water as a solvent was an appropriate choice for our study. In consequence, we also focused on the water-solube BrC light absorption. To assess the contribution to the total BrC light absorption, Aethalometer measurements were included into the study.
For forthcoming studies, however, organic solvents are also considered to include less water-soluble BrC constituents, like the mentioned oligomers.

3. Levoglucosan:
Since levoglucosan was quantified using IC coupled to PAD, how confident are the authors that there are no co-eluting species? I ask this question since GC/MS with prior derivatization tends to take this concern away due to its high chromatographic resolution.

The method used in this study to determine levoglucosan has been published as Iinuma et al. 2009. In this publication, it was stated that the method enables the separation of levoglucosan and arabitol, which was an issue in previous studies. Furthermore, an intercomparison study by Yttri et al. 2015 (Atmos. Meas. Tech.) showed that the used method (high-performance anion-exchange chromatography (HPAEC) with pulsed amperometric detection (PAD))

delivers comparable results as methods using GC/MS. Therefore, we are confident that this data is reliable.

4. Changing the pH of aqueous extracts:
By intentionally making extracts acidic or basic, do the authors fear changes in the chemical composition could occur due to unwanted reactions? This is important to think about, especially if one is concerned about the presence of oligomeric species that could degrade via dehydration reactions or other types of unforeseen reactions. I think the authors need to comment on this potential issue. As an example, how might this affect the UV-Vis measurements? I can see this step you have introduced here being confusing to some of the readership of ACP.

This step was introduced to investigate the NACs and their contribution to the light absorption in an environment where they are either fully protonated or deprotonated. Without this step, a mixture of protonated and deprotonated forms would have been present in the solution. By introducing a change in pH, the upper and lower limits for the contribution of NACs to the BrC light absorption could be determined. To minimize the risk of potential chemical modification the solutions where kept in the dark and analyzed as soon as possible after preparation by UV-Vis-spectrophotometry.
For more clarity, an additional text was added to the Section 2.4 in the manuscript (p. 6, l. 4):

"to obtain the lower and upper limit for the contribution of NACs to the BrC light absorption. In principle, it could be possible that introducing acids or bases into the system induces unforeseen chemical reactions influencing the total light absorption of the aqueous extract. However, To minimize the risk of potential chemical modification the solutions where kept in the dark and analyzed as soon as possible after preparation by UV-Vis-spectrophotometry."

5. BB not the possible source of NACs at the Chinese sites:

Were these NACs during summer in China associated with the photochemical oxidation of anthropogenic VOCs, such as aromatics? Previous work, such as by the EPA group (Jaoui et al., studies) and Sato et al. (JPCA, 2008), have shown that the photochemical oxidation of aromatic VOCs in the presence of NOx yields NACs. If you collect filters from these experiments, they are brown. So it would be interesting to know if this is correlated with photochemical processing of VOCs (like aromatics) associated with traffic emissions.

Thank you very much for this comment. From our field experiments alone, it is difficult to attribute concrete sources to the observed NAC concentrations. Unfortunately, there is no VOC data available. Mentioned possible sources in the manuscript are therefore very speculative. Nevertheless, NACs may derive from photochemical processing of VOCs transported to the site. Hence, according to the referee's suggestion this possible source was added to Section 3.2.
"*It was found that NACs can be a product of the photochemical processing of anthropogenic volatile organic compounds (Jaoui et al. 2008), which might be a possible source for NACs at the Chinese sites besides BB." was added to the text. (p.10, l. 39)*

Additional reference:
"Jaoui, M., Edney, E. O., Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., Surratt, J. D., and Seinfeld, J. H.: Formation of secondary organic aerosol from irradiated α-pinene/toluene/NOx mixtures and the effect of isoprene and sulfur dioxide, J. Geophys. Res., 113, D09303, doi: 10.1029/2007JD009426, 2008."

6. Page 10, Line 26:

The authors state "nighttime concentrations were found to be slightly higher than during the day." For statements like this one and elsewhere in the manuscript, is this statistically significant?

We checked the data using the t-test method and the slightly higher concentrations observed at nighttime were found to be not statistically significant. To clarify the remark "(not statistically significant at 95 % confidence level)" was added to the text (p. 10, l. 26).
The manuscript was checked for similar statements. In other instances in the manuscript, where comparisons where made, clear differences where seen in the data set. In this cases, the information of the statistically significance was not added.

7. Page 11, Line 11:
The authors state "The contribution of NACs to Abs(370 nm) was low for the campaigns Waldstein (summer) and Melpitz (summer)." Probably not unexpected, right, especially since there is no BB influence or traffic influence? But are there other types of BrC constituents missing, such as those observed from monoterpenes in lab studies by the Laskin and Nizorodov groups? It would be interesting to know what is contributing to the small BrC levels.

We agree to the referee's comment. Since the focus of this study was on NACs, we cannot provide further information of BrC constituents derived from biogenic emission from our data set. However, a possible source for the observed light absorption, mentioned in the literature, was added to Section 3.3.

Additional text:
p. 11, l. 13:
"This result is not surprising, due to the low influence of BB aerosols or traffic and thus low NAC concentrations. A recent study by Nguyen et al. 2013 suggested the formation of BrC from ketoaldehydes derived from biogenic monoterpenes in the presence of ammonium ions. Thus, this reaction may play a role in regions with higher influence of biogenic emissions and might be one explanation for the observed absorption at the Melpitz (summer) and Waldstein (summer) campaigns. The formed species were suggested to consist of conjugated aldol condensates, secondary imines and nitrogen containing heterocycles."

Additional reference:
"Nguyen, T. B., Laskin, A., Laskin, J., and Nizkorodov, S. A.: Brown carbon formation from ketoaldehydes of biogenic monoterpenes, Faraday Discuss., 165, 291-315, doi: 10.1039/C3FD00036B, 2013."

8. Fix the numbering of subsections in Section 2.
The numbering was fixed.

Literature:

Iinuma, Y., Engling, G., Puxbaum, H., and Herrmann, H.: A highly resolved anion-exchange chromatographic method for determination of saccharidic tracers for biomass combustion and primary bio-particles in atmospheric aerosol, Atmos. Environ., 43, 1367-1371, doi: 10.1016/j.atmosenv.2008.11.020, 2009.

Teich, M., van Pinxteren, D., and Herrmann, H.: Determination of nitrophenolic compounds from atmospheric particles using hollow-fiber liquid-phase microextraction and capillary electrophoresis/mass spectrometry analysis, Electrophoresis, 35, 1353-1361, doi: 10.1002/elps.201300448, 2014.

Yttri, K. E., Schnelle-Kreis, J., Maenhaut, W., Abbaszade, G., Alves, C., Bjerke, A., Bonnier, N., Bossi, R., Claeys, M., Dye, C., Evtyugina, M., García-Gacio, D., Hillamo, R., Hoffer, A., Hyder, M., Iinuma, Y., Jaffrezo, J.-L., Kasper-Giebl, A., Kiss, G., López-Mahia, P. L., Pio, C., Piot, C., Ramirez-Santa-Cruz, C., Sciare, J., Teinilä, K., Vermeylen, R., Vicente, A., and Zimmermann, R.: An intercomparison study of analytical methods used for quantification of levoglucosan in ambient aerosol filter samples, Atmos. Meas. Tech., 8, 125-147, doi:10.5194/amt-8-125-2015, 2015.