

Response to the Anonymous Referee's

We greatly appreciate the comments and suggestions of the three referees, which helped to improve our manuscript. We thoroughly revised the manuscript according to the referee's suggestions.

In the following, the referee's comments are given in plain text. Our response and made revisions are given in italic. The lines and pages are given according to the submitted ACPD manuscript.

Further corrections on the manuscript are listed below the replys to the referees comments.

Response to Anonymous Referee #1

This paper is investigating the concentrations of nitrated aromatic compounds (NACs) in aerosols collected in Germany and China during winter and summer seasons. The contribution of these compounds to the light absorption of BrC PM and water extracts was determined and discussed. This paper is scientifically very interesting and important for understanding the contribution of individual BrC compounds to the light absorption properties of atmospheric aerosols. The manuscript is well written and I have only a few major and minor comments.

The authors would like to thank the reviewer for recommending the paper and the helpful comments. The revision was carried out carefully according to the reviewer's suggestions.

1. Major comment 1. UV-Vis spectra of WSOC fractions were recorded from 300 to 800 nm, however, only 370 nm wavelength was used in the present study (to compare the data with Aethalometer measurements). Different aromatic compounds can have different spectra (see Pretsch et al. 2008, Samburova et al. 2016) and thus their contribution to the BrC absorptivity can vary based on wavelength. It would be very interesting to see how eight NACs contribute to the light absorption of aqueous filter extracts over the spectrum range between 300 and 800 nm.

Thank you very much for this comment. We agree, that the contribution of NACs to the aqueous extract light absorption over the spectrum range of 300 to 800 nm might be interesting to the reader. Therefore, according to the suggestion of the referee, we added a new diagram to the main script showing the contribution of NACs to Abs over the spectral range of 300 to 500 nm (acidic conditions). This range was chosen, since above 500 nm NACs are only weakly absorbing. A short description of the diagram was added to the text in Section 3.3. Furthermore, a diagram for the contribution of NACs to Abs over 300 to 500 nm under alkaline conditions, as well as the spectral evolution of Abs under acidic and alkaline conditions was added to the supplement.

Detailed changes to the manuscript:

Additional text added to Section 3.3 (lines and pages are given according to the submitted ACPD manuscript)

p. 11, l. 7:

“The focus is on the relative contribution to the aqueous extract light absorption at the wavelength of 370 nm to match the 370 nm channel of the Aethalometer. To give additional information, the relative contribution of NACs to Abs (acidic conditions) over a spectral range of 300 to 500 nm is presented in Fig. 5 as their campaign averages.”

p. 11, l. 18:

“The relative contribution of NACs to Abs is wavelength dependent. Under acidic conditions, the contribution of NACs to the aqueous extract light absorption increases towards lower wavelength, reaching a maximum that was found to generally lie in the range of 330 - 350 nm (see Fig. 5). Moreover, it can be seen that maximum values differ for individual compounds. Under alkaline conditions, this maximum shifts towards the range of 400 - 420 nm (see Fig. S6). As stated above, the results for acidic conditions are likely to be more atmospherically relevant. Therefore, a higher influence of NACs towards shorter wavelengths suggests that they can be more important in terms of their influence on atmospheric photochemistry, e.g. O₃ photolysis (Jacobson, 1999).”

removed sentence:

p. 12, l. 10-11:

“This suggests that the influence of NACs is higher towards shorter wavelength, i.e. near their absorption maximum and thus can be more important in terms of their influence on atmospheric photochemistry, e.g. O₃ photolysis (Jacobson, 1999).”

Additional diagram in the manuscript:

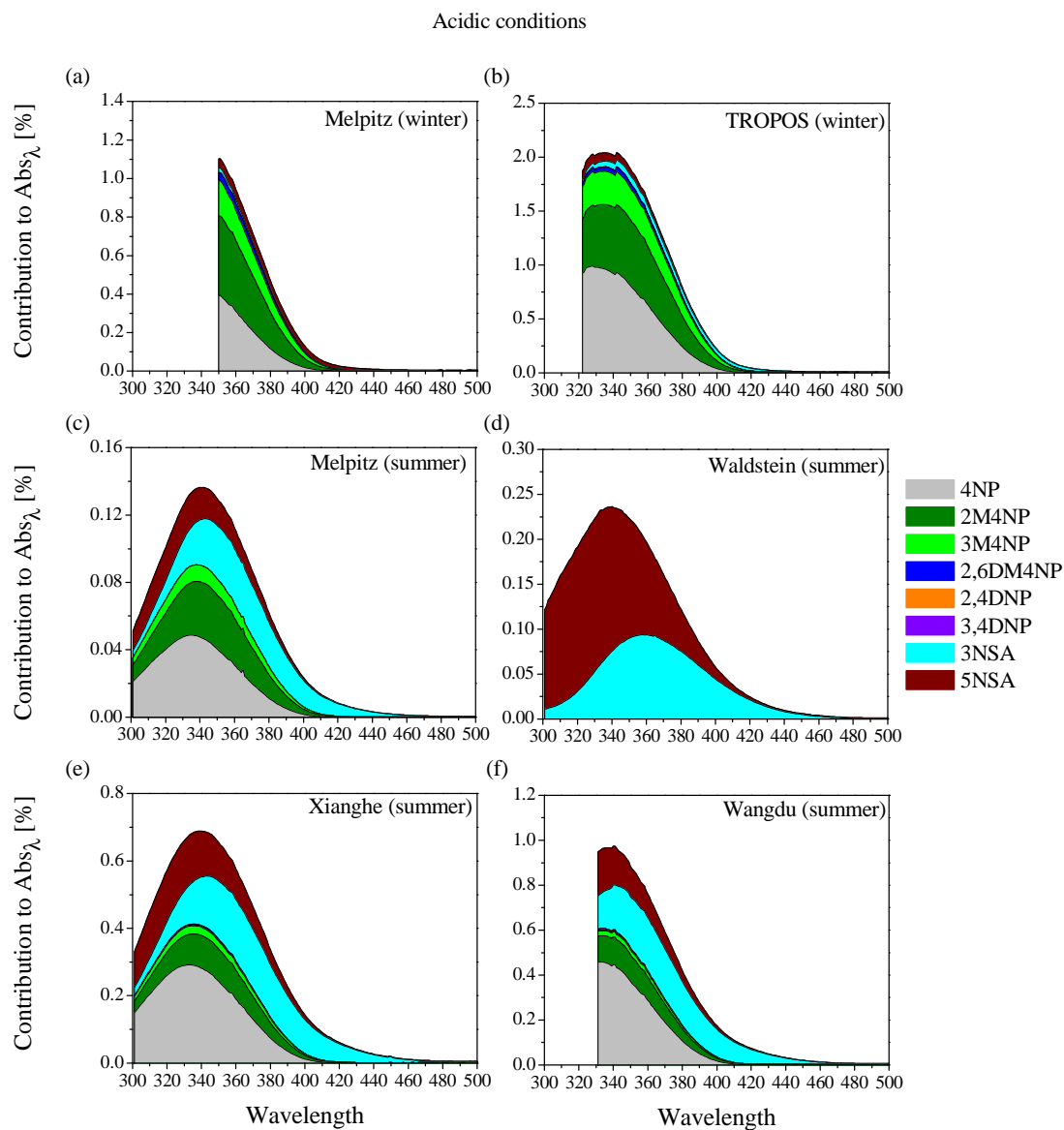


Figure 5. Relative contribution of NACs to Abs_{λ} over the spectral range of 300 to 500 nm for each measurement campaign (a-f) under acidic conditions. The data is presented as campaign averages. Due to instrumental issues, data for lower wavelengths is not always available.

Figure numbers of diagram appearing later in the text were changed accordingly.

Additional diagrams in the supplement:

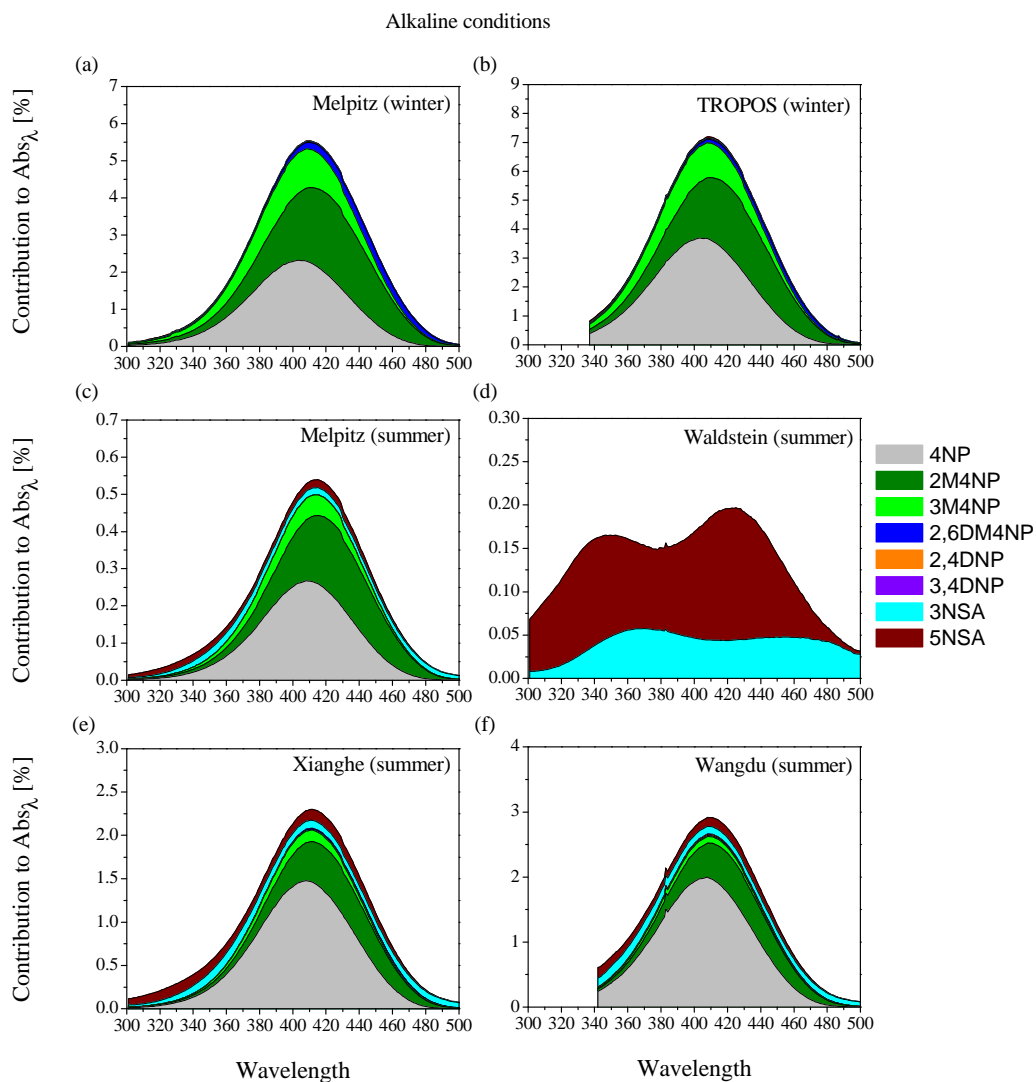


Figure S6. Relative contribution of NACs to Abs_{λ} over the spectral range of 300 to 500 nm for each measurement campaign (a-f) under alkaline conditions. The data is presented as campaign averages. Due to instrumental issues, data for lower wavelengths is not always available.

Acidic conditions

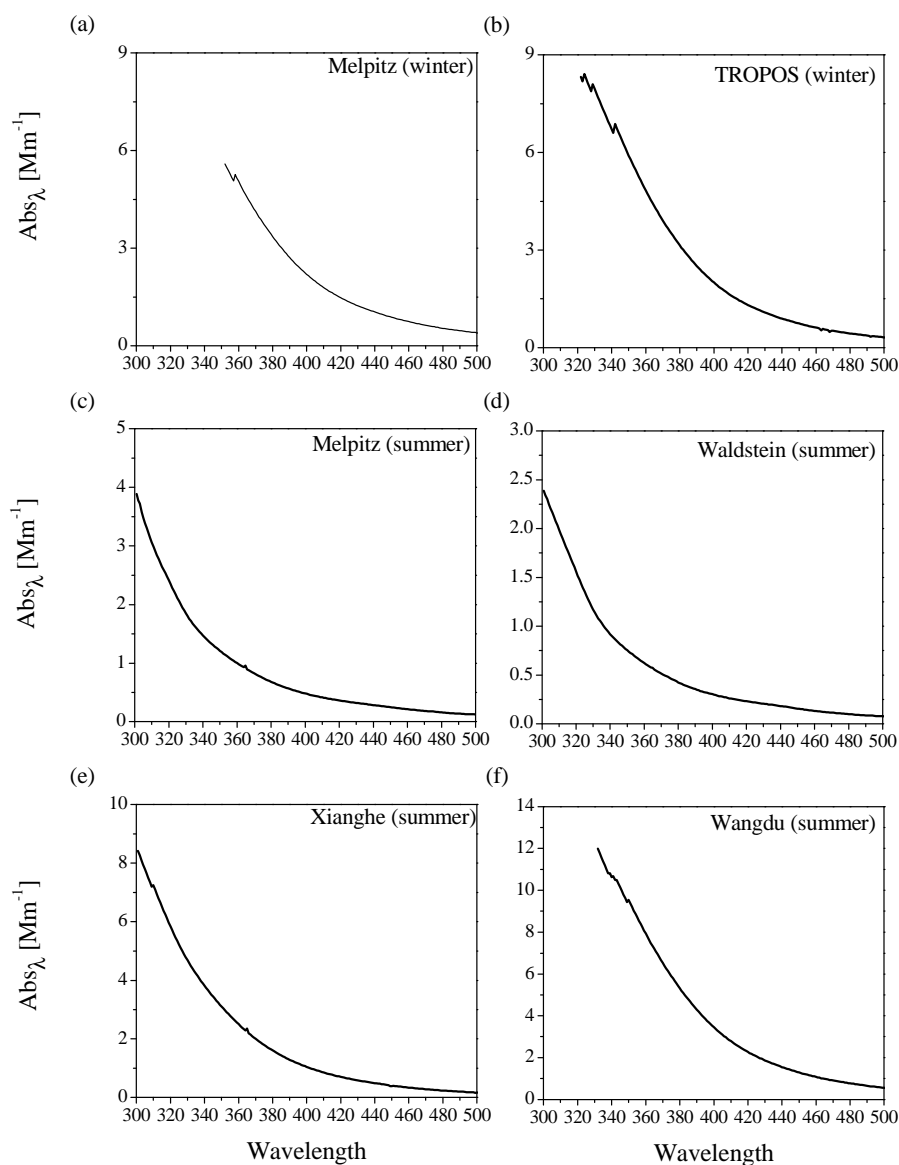


Figure S7. Abs_{λ} over the spectral range of 300 to 500 nm for each measurement campaign (a-f) under acidic conditions. The data is presented as campaign averages. Due to instrumental issues, data for lower wavelengths is not always available.

Alkaline conditions

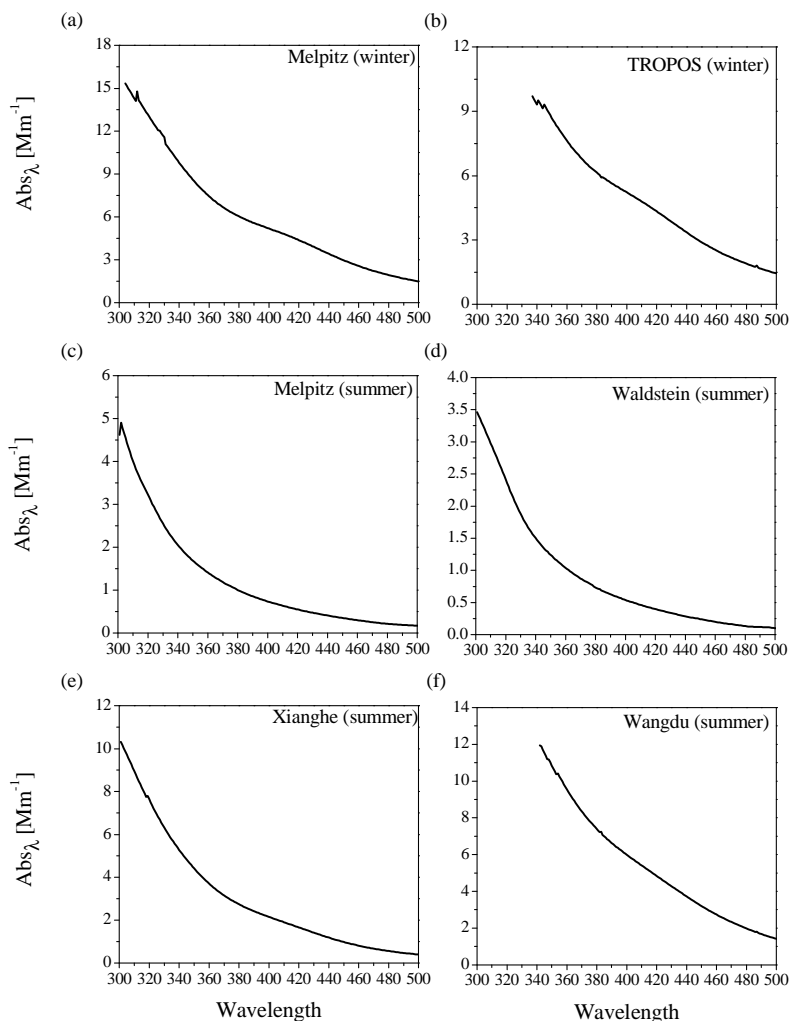


Figure S8. Abs_{λ} over the spectral range of 300 to 500 nm for each measurement campaign (a-f) under alkaline conditions. The data is presented as campaign averages. Due to instrumental issues, data for lower wavelengths is not always available.

2. Major comment 2. Did the author compare the absorption properties of PM water extracts at “natural” pH with artificially acidified and alkylated samples?

The pH of the pure water extracts depends on the amount of water used in the extraction process. Furthermore, it would contain a mixture of protonated and deprotonated NACs. To determine the relative contribution of NACs to Abs one would need to know the amount of protonated and deprotonated species in the solution. Under the chosen acidic conditions the NACs are fully protonated and under alkaline conditions fully deprotonated. Thus we determined the lower and upper limits for the contribution of NACs to Abs. Due to the limited amount of aqueous filter extracts (and filter material) we chose to analyse acidified and alkalinized filter extracts only.

3. Minor comments: Abstract, Line 13. Use (NACs: nitrophenols and nitrated salicylic acid)
P. 2, Line 26. “in the UV” means in the “UV-Vis range of the spectrum”?

Here, we do refer to the “UV range of the spectrum” and not to the “UV-Vis range of the spectrum, since the observed reduction of photolysis rates and atmospheric oxidants was reported to be in the UV and not UV-Vis. However, to clarify this sentence “range of the spectrum” was added.

4. P.2, Line 35. Use “BC” instead of “black carbon”, since this abbreviation was introduced above (line 18)

P. 10, Line 23. Use abbreviation “NPs” P. 10, Line 40. Use abbreviation “NACs”

Changes were made according to the referee’s suggestion throughout the manuscript.

5. P. 3, Lines 6-7. References are needed after “. . .absorption at 365 nm is used to characterize water-soluble BrC.”

References added “(e.g., Bosch et al. 2014; Cheng et al. 2011; Hecobian et al. 2010)” (These references were already listed in the reference list in the manuscript)

6. P. 3, Line 33. Use “biomass-burning aerosols”

done

7. P. 3, Lines 41-43. This long sentence is a little confusing.

To clarify this part, the sentences was divided into two sentences: “The present study aims to expand the understanding of BrC and water-soluble BrC by investigating its spatial and temporal variation in different, very diverse environments (urban, rural, biogenic, high BB influence). Furthermore, the contributions of individual light-absorbing organic compounds to the BrC light absorption is included.”

8. P4, Line 9. Add the period (not “until 31 January”) for “the first half of the campaign”.

replaced with “(24 to 31 January)”

9. P4, Line 41. It sounds a little better, but optional: “Analysis of WSOC, levoglucosan, NACs and UV/Vis spectrophotometry measurements were carried out using aqueous filter extracts of different portions of filter in ultrapure water.”

This sentence was adopted to the manuscript according to the referee’s suggestion

10. P. 10, paragraph 1. Why significant BB absorption was observed at the German sites during winter campaigns (because there are more domestic biomass-burning events)?

As stated in Section 2.1, we concluded that BB was playing a major role at the German winter sites because of high observed levoglucosan concentrations. It is also known that BB due to domestic heating can play a large role in this area.

11. P.10, Lines 35-39. If BB was not the major contributor to the analyzed BrC particles, what was a possible source of BrC compounds? Suggestions?

A similar question was asked by the anonymous Referee#2. Based on the comment by the anonymous Referee#2 and anonymous Referee#1 a possible source for NACs was added to Section 3.2.

Added text:

p.10, l. 39:

“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.

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/NO_x mixtures and the effect of isoprene and sulfur dioxide, *J. Geophys. Res.*, 113, D09303, doi: 10.1029/2007JD009426, 2008.”*

12. P.11, Line 41. Delete space between 4 and % Summary: I recommend this manuscript for publication after minor revisions.

Already published papers in ACP do use a space between the number and %. Therefore, we chose to also use a space between the number and % and the corrections were made accordingly throughout the text.

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):

“PM₁₀ was collected on quartz fiber filters with a Digital 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 study 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-soluble 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 arabinol, 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 were 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 were 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 NO_x 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/NO_x 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 were made, clear differences were seen in the data set. In this cases, the information of the statistical 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 Nizkorodov 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., Evtugina, 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.

Response to Anonymous Referee #3

General comments

The authors present quantitative data on concentrations and light absorption contributions of eight nitrated aromatic compounds (NACs) measured in atmospheric particles at five different locations in Germany and China during two different seasons. Light absorption by brown carbon is an important topic for the overall assessment of the direct aerosol effect; many open questions remain related to the extent and organic compounds involved. The diversity of measurement sites and the comparison of two different methods for light absorption assessment make this study very interesting. The manuscript is well written. I thus recommend publication after the comments below have been addressed.

We would like to thank the referee for the recommendation and the helpful suggestions

Specific comments

1. The focus is on WSOC and water-soluble BrC. What I am missing is an assessment/estimate of the fractions WSOC/OC and water-soluble BrC/BrC, to get an idea of comparability and validity of methods. I am also missing a direct comparison of babs, the light absorption coefficient of particles, and Abs, and as well the calculated MAE (why was MAE not calculated for the Aethalometer data, based on babs and total PM mass/total PM organic mass, if available?) At least a comparison plot of the relative temporal evolution of these parameters

for the Waldstein (summer) and TROPOS (winter) campaigns is highly interesting from both a scientific and methodological point of view and should be added to the paper (could also be in the SI).

*We agree, that this information might be interesting to the reader. Therefore, as suggested by the referee, a diagram was added to the supplement containing the temporal variation of MAE₃₇₀ for particulate BrC, the fraction WSOC/OC and the fraction of aqueous extract light absorption to particulate BrC light absorption for the campaigns TROPOS (winter) and Waldstein (summer). Abs and b_{abs} are not directly comparable. According to the method by Liu et al. 2013 (*Atmos. Chem. Phys*) a conversion factor of 2 was applied to Abs. A brief comparison of Abs and b_{abs} is given in Section 3.1.3.*

Additional text:

p. 9, l. 2:

“Normalizing the determined babs for particulate BrC by the according OC content gives the mass absorption efficiency for BrC in the particle ($MAE_{370, BrC, particle}$). The temporal variation of $MAE_{370, BrC, particle}$ is displayed in Fig. S4.”

p. 9, l. 8

“and an average $MAE_{370, BrC, particle}$ of $1.95 \text{ m}^2 \text{ g}^{-1}$ was calculated”

p. 9., l. 19:

“, a $MAE_{370, BrC, particle}$ of $0.21 \text{ m}^2 \text{ g}^{-1}$ ” and “The temporal variation of the fraction of the converted Abs_{370} to the particulate BrC light absorption is given in Fig. S4.”

Additional diagrams in the supplement:

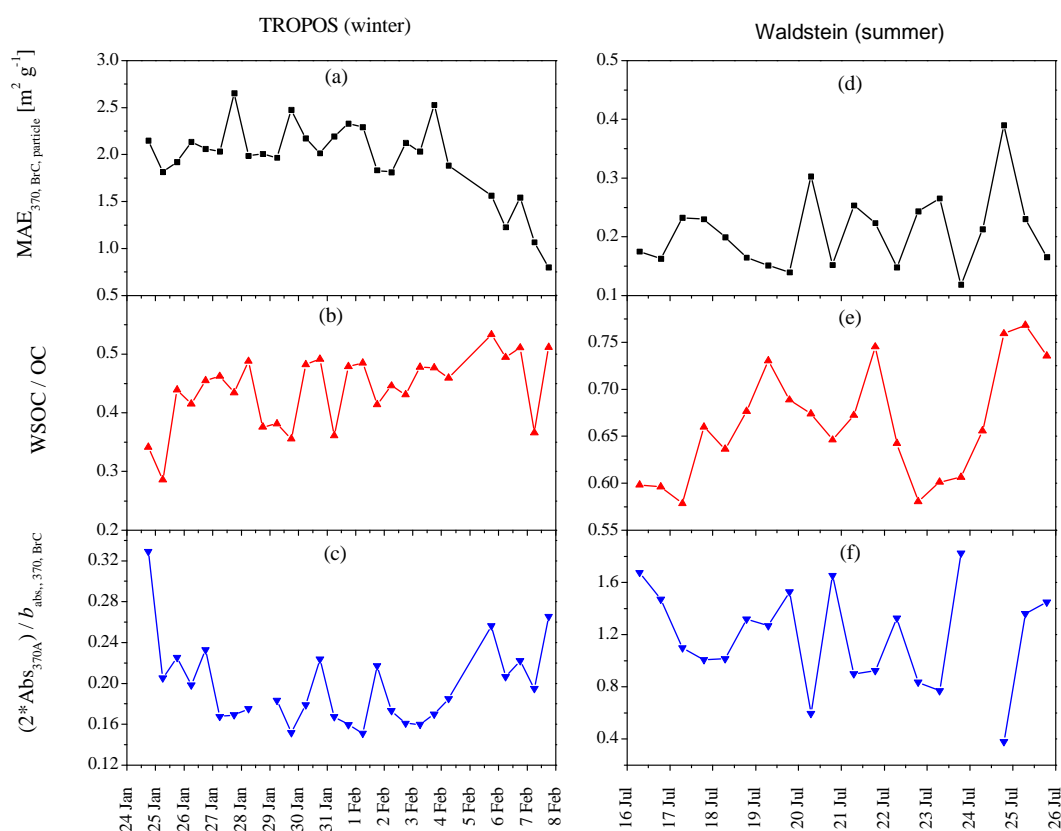


Figure S4. Temporal variation of $MAE_{370, BrC, particle}$ for particulate BrC, the $WSOC/OC$ fraction and the fraction of aqueous extract light absorption to particulate BrC light absorption for the campaigns TROPOS (winter) (a-c) and Waldstein (summer) (d-f). For comparability of aqueous extract light absorption and the particulate BrC light absorption, Abs_{370A} (acidic conditions) was multiplied by a factor of 2, according to the method mentioned in the main text. $MAE_{370, BrC, particle}$ was determined by normalizing $b_{abs, 370, BrC}$ by the according OC content of the sample.

2. P. 2, l. 14 – 15: With the attention brown carbon is getting in recent years (and in the rest of your introduction) this statement seems too strong here. Add “in global climate models” for specification.

Additions were made according to the referee’s suggestions.

Additional text:

p. 2., l. 14:

“in global climate models”

3. P. 3, l. 3: To my knowledge, Sandradewi et al. (Environ. Sci. Technol., 2008, 42 (9), pp 3316–3323, DOI: 10.1021/es702253m) were among the first to introduce the “Aethalometer model” for the separation of BC and BrC (then traffic vs wood burning contributions). Please cite.

Additions were made according to the referee’s suggestions.

Additional text:

p. 3, l. 3

“Sandradewi et al. 2008”

Additional reference:

“Sandradewi, S., Prevot, A. S. H., Szidat, S., Perron, N., Alfarra, M. A. Lanz, V. A., Weingartner, E., and Baltensperger, U.: Using Aerosol Light Absorption Measurements for the Quantitative Determination of Wood Burning and Traffic Emission Contributions to Particulate Matter, Environ. Sci. Technol., 42, 3316-3323, doi: 10.1021/es702253m, 2008.”

4. P. 4, l. 9 (compare comment for Table 1 and p. 4, l. 38 - 40): Give time interval for 12h mean.

see reply to 10.

5. P. 4, l. 33: How were they determined, based on what criteria? Please add this information.

The determination of NACs was explained later in the text. To avoid confusion, specific NAC compounds are now mentioned later in the text

p. 4, l. 33 - 36 were moved to p. 5, l. 13.

6. P. 10, l. 27 - 30: Photolysis can be sink of NP as well.

“or photolysis processes” added to p. 10, l. 28.

Technical comments:

7. The abstract is relatively long and dense. It would profit from a bit of streamlining. Consider moving the sentence on p. 1, l. 34 – 24, to l. 34.

As suggested by the referee, to improve the readability, the abstract was shortened.

Additional text:

p.1, l. 25

“with larger values at higher pH”

Removed sentences:

p. 1, l. 25 - 26:

“: at pH 10, the aqueous light absorption coefficient Abs_{370} and the mass absorption efficiency (MAE_{370}) at 370 nm were a factor of 1.6 and 1.4 larger than at pH 2, respectively”

p. 1. l. 29 - 31:

“Furthermore, it was found that the MAE_{370} values in 30 winter in Germany exceeded those of the Chinese summer background stations (average of $0.85 \pm 0.24 \text{ m}^2 \text{ g}^{-1}$ compared to $0.47 \pm 0.15 \text{ m}^2 \text{ g}^{-1}$)”

p. 1. l. 36 - p. 2. l. 1:

“The absorption Ångström exponent of the ambient aerosol during the campaigns at TROPOS (winter) and Waldstein (summer) was found to be 1.5 ± 0.1 and 1.2 ± 0.3 , respectively.”

p. 2, l. 8 - 9:

“A correlation of NAC concentrations with Abs_{370} was observed for the BB-influenced campaigns at TROPOS (winter) and Melpitz (winter).”

8. P. 2, l. 14: [. . .] are usually treated [. . .]

corrected

9. P. 5, l. 7: What do you mean by “distributed sources”? Not clear.

Here, we meant it in the sense of “various” or “different”. For clarity the word “distributed” was replaced by “various”

10. Table 1: The alignment of some of the columns is off. Please correct for better readability. Also add the sampling times (now give in Table S2) to Table 1.

Table 1 was corrected and the sampling times were added. Table S1, that originally contained the sampling times, was removed from the supplement.

11. Table 2: I suggest highlighting the highest and lowest values in each column/category. The light absorption contribution (in %) is given for NP and NSA individually, but there is not further mentioning of this. I assume NP is the sum of the 6 NP and NSA the sum of the 2 NSA you mention on p. 4, l. 33 -35. This kind of differentiation/grouping is only done in Table 2 – I suggest making that consistent throughout the manuscript. Do A) and B) refer to acidic and alkaline conditions? Please clarify and add this information in the table caption.

“Acidic conditions are indicated by the letter “A” and alkaline conditions are indicated by the letter “B”” was added to the table caption.

As mentioned by the referee, the differentiation for NPs and NSAs was made in Table 2 only. To be consistent with the text, we changed the information in Table 2 to values for NACs instead NPs + NSAs. Furthermore the highest and lowest mean values for each category were marked in bold, as suggested by the referee.

Literature

Liu, J., Bergin, M., Guo, H., King, L., Kotra, N., Edgerton, E., and Weber, R. J.: Size-resolved measurements of brown carbon in water and methanol extracts and estimates of their contribution to ambient fine-particle light absorption, *Atmos. Chem. Phys.*, 13, 12389-12404, doi: 10.5194/acp-13-12389-2013, 2013.

Additional changes to the manuscript:

- the manuscript was checked for spelling and grammar mistakes
- Figure 4 was redesigned for a better readability of the diagram

Contributions of nitrated aromatic compounds to the light absorption of water-soluble and particulate brown carbon in different atmospheric environments in Germany and China

Monique Teich¹, Dominik van Pinxteren¹, Michael Wang², Simonas Kecorius¹, Zhibin Wang^{1,5},

Thomas Müller¹, Griša Močnik^{3,4}, Hartmut Herrmann¹

¹Leibniz Institute for Tropospheric Research, TROPOS, 04315 Leipzig, Germany

²McMaster University, Hamilton, ON L8S 4L8, Canada

³Aerosol d.o.o., 1000 Ljubljana, Slovenia

⁴Condensed Physics Department, Jožef Stefan Institute, Ljubljana, Slovenia

⁵Now at: Multiphase Chemistry Department, Max Planck Institute for Chemistry, 55128 Mainz, Germany

Correspondence to: Hartmut Herrmann (hartmut.herrmann@tropos.de)

Abstract. The relative contribution of eight nitrated aromatic compounds (NACs; nitrophenols and nitrated salicylic acids) to the light absorption of aqueous particle extracts and particulate brown carbon were determined from aerosol particle samples collected in Germany and China.

High-volume filter samples were collected during six campaigns, performed at five locations in two seasons: (I) two campaigns with strong influence of biomass burning (BB) aerosol – at the TROPOS institute (winter, 2014, urban background, Leipzig, Germany) and the Melpitz research site (winter, 2014, rural background); (II) two campaigns with strong influence from biogenic emissions – at Melpitz (summer, 2014) and the forest site Waldstein (summer, 2014, Fichtelgebirge, Germany), and (III) two CAREBeijing-NCP campaigns – at Xianghe (summer, 2013, anthropogenic polluted background) and Wangdu (summer, 2014, anthropogenic polluted background with a distinct BB-episode), both in the North China Plain.

The filter samples were analyzed for NAC concentrations and the light absorption of aqueous filter extracts was determined. Light absorption properties of particulate brown carbon were derived from a seven-wavelength Aethalometer during the campaigns at TROPOS (winter) and Waldstein (summer). The light absorption of the aqueous filter extracts was found to be pH dependent, with larger values at higher pH. In general, Abs_{370} and the mass absorption efficiency (MAE_{370}) at 370 nm were a factor of 1.6 and 1.4 larger than at pH 2, respectively. In general, Abs_{370} ranged from 0.21–21.8 Mm^{-1} under acidic conditions and 0.63–27.2 Mm^{-1} under alkaline conditions, over all campaigns. The observed MAE_{370} was in a range of 0.10–1.79 $m^2 g^{-1}$ and 0.24–2.57 $m^2 g^{-1}$ for acidic and alkaline conditions, respectively. For MAE_{370} and Abs_{370} , the observed values were higher in winter than in summer, in agreement with other studies. Furthermore, it was found that the MAE_{370} values in winter in Germany exceeded those of the Chinese summer background stations (average of $0.85 \pm 0.24 m^2 g^{-1}$ compared to $0.47 \pm 0.15 m^2 g^{-1}$). The lowest MAE was observed for the Waldstein (summer) campaign (average of $0.17 \pm 0.03 m^2 g^{-1}$), indicating that freshly emitted biogenic aerosols are only weakly absorbing. In contrast, a strong relationship was found between the light absorption properties and the concentrations of levoglucosan, corroborating findings from other studies.

Regarding the particulate light absorption at 370 nm, a mean particulate light absorption coefficient $b_{abs,370}$ of 54 Mm^{-1} and 6.0 Mm^{-1} was determined for the TROPOS (winter) and Waldstein (summer) campaigns, respectively, with average contributions of particulate brown carbon to $b_{abs,370}$ of 46% at TROPOS (winter) and 15% at Waldstein (summer). The absorption Ångström exponent of the ambient aerosol during the campaigns at TROPOS (winter) and Waldstein (summer) was found to be 1.5 ± 0.1

and 1.2 ± 0.3 , respectively. Thus, the Aethalometer measurements support the findings from aqueous filter extracts of only weakly absorbing biogenic aerosols in comparison to the more polluted and BB influenced aerosol at TROPOS (winter).

The mean contribution of NACs to the aqueous extract light absorption over all campaigns ranged from 0.10 %–1.25 % under acidic conditions and 0.13 %–3.71 % under alkaline conditions. The high variability among the measurement sites showed that the emission strengths of light absorbing compounds and the composition of brown carbon were very different for each site. The mean contribution of NACs to the particulate brown carbon light absorption was 0.10 ± 0.06 % (acidic conditions) and 0.13 ± 0.09 % (alkaline conditions) during the Waldstein (summer) campaign and 0.25 ± 0.21 % (acidic conditions) and 1.13 ± 1.03 % (alkaline conditions) during the TROPOS (winter) campaign. ~~A correlation of NAC concentrations with Abs_{320} was observed for the BB-influenced campaigns at TROPOS (winter) and Melpitz (winter).~~

The average contribution of NACs to the aqueous extract light absorption over all campaigns was found to be 5 times higher than their mass contribution to water-soluble organic carbon indicating that even small amounts of light-absorbing compounds can have a disproportionately high impact on the light absorption properties of particles.

1. Introduction

Organic components of atmospheric aerosols are usually treated as solely light scattering in global climate models over the near-ultraviolet and visible range (UV/Vis) of the solar spectrum and therefore only make a negative contribution to radiative forcing (Feng et al., 2013). However, the existence of light absorbing organic carbon (OC) has become more and more evident in the past decade and can be a regionally important phenomenon (see reviews of Andreae and Gelencser (2006) and, more recently, Laskin et al. (2015) and references therein and Ulevicius et al. (2010)). In contrast to black carbon (BC), which absorbs light efficiently over the whole visible and UV region, light absorption by OC exhibits a distinct wavelength dependence. The light absorption sharply increases with decreasing wavelength, making it an efficient absorber in the UV/Vis range. Due to its characteristic yellowish to brownish color, light absorbing OC is also often addressed as brown carbon (BrC). The light absorption by BrC over the whole solar spectrum are found to be relatively weak compared to BC (Liu et al., 2013a). Nevertheless, at near UV/Vis wavelengths (300–500 nm) BrC has a non-negligible effect on radiative forcing and the regional and global climate (e.g., Bahadur et al., 2012; Feng et al., 2013; Jo et al., 2016; Park et al., 2010). For instance, modelling studies showed that the radiative forcing of BrC relative to BC is up to 25 % (Feng et al., 2013). Furthermore, BrC light absorption in the UV range of the spectrum may alter the concentrations of atmospheric oxidants due to reduced photolysis rates (Jacobson, 1999).

The light absorption of ambient particles is generally quantified by the determination of the particulate light absorption coefficient b_{abs} , (in Mm^{-1}), which can be normalized by the sample mass to give the mass absorption efficiency (MAE in $m^2 g^{-1}$). Mass absorption efficiencies MAE can then further be used to estimate the radiative forcing of particulate BrC, which makes it an important parameter for modelling studies. These models start with modeled emitted mass, which is converted into concentrations using a dispersion model. The absorption of aerosols in the atmosphere is then determined using the appropriate MAE (Feng et al., 2013). The wavelength dependence of light absorption of a particle sample is described by the absorption Ångström exponent (AAE) based on the power-law dependence of b_{abs} :

$$\frac{b_{abs,\lambda_1}}{b_{abs,\lambda_2}} = \left(\frac{\lambda_1}{\lambda_2}\right)^{-AAE}, \quad (1)$$

~~BC~~ Black carbon has a weak wavelength dependence and often an AAE of 1.0 is assumed, which is the Mie theoretical value, though measured values range between 0.8–1.1 (Gyawali et al., 2009). Values greater than 1.1 indicate a stronger wavelength dependence, and give evidence for the presence of absorbers at lower wavelengths, such as BrC but also mineral dust (Wang et al., 2013).

Several methods exist to quantify the light absorption properties of BrC. Filter-based and multi-wavelength measurement techniques are commonly used to assess the contribution of BrC to the total aerosol light absorption (Moosmüller et al., 2009).

One of these instruments is the seven-wavelength Aethalometer, which operates from 370 nm to 940 nm. Due to the main light absorption of BrC at short wavelengths, the 370 nm channel is of particular interest. To estimate the contributions of BrC and BC to aerosol light absorption, a simple approach based on wavelength pairs and assumed AAEs to distinguish between the light absorption of BC and BrC has often been used (Lack and Langridge, 2013; [Sandradewi et al. 2008](#)).

Another method is to extract aerosol particles into solvents, mostly water or methanol (e.g., Bosch et al., 2014; Chen and Bond, 2010; Cheng et al., 2011; Liu et al., 2013a). The advantage of this approach is that BC is insoluble in these solvents and therefore removed by filtration. The extracts are then further analyzed by UV/Vis spectrophotometry. Commonly, light absorption at 365 nm is used to characterize water-soluble BrC (e.g., Bosch et al. 2014; Cheng et al. 2011; Hecobian et al. 2010). This wavelength is in a range where the light absorption of inorganics does not interfere, whereas the light absorption of organics shows a sufficiently high intensity (Hecobian et al., 2010). Observed MAE values (related to the water-soluble OC, WSOC) for water-soluble BrC typically range between 0.41 and 1.80 m² g⁻¹ (Cheng et al., 2016; Hecobian et al., 2010), where higher values are usually found in winter.

Up till now, field measurements of the light absorption properties of water-soluble BrC have been performed mostly in the US and Asia, and measurements in Europe are scarce. Duarte et al. (2005) investigated the optical properties of WSOC from aerosol samples collected at a rural site in Portugal. They found a seasonal variation with a higher absorptivity in autumn than in summer. Some studies have reported the optical properties of humic-like substances (HULIS), which are a part of WSOC (e.g., Baduel et al., 2010; Utry et al., 2013).

Sources of BrC are very diverse. Known primary sources are biomass burning (BB, Kirchstetter and Thatcher, 2012; Lack et al., 2013; Mohr et al., 2013), and fossil fuel and residential coal combustion (Bond, 2001; Olson et al., 2015). Moreover, BrC can be produced by secondary reactions of anthropogenic (Lin et al., 2015a; Nakayama et al., 2010) or biogenic precursors (Flores et al., 2014; Kampf et al., 2012; Lin et al., 2014).

The molecular composition of BrC still remains largely unknown due to its complex nature. Several attempts have been made to characterize BrC at a molecular level (Lin et al., 2015a, 2015b). Among the identified compound groups are large macromolecules, like HULIS (Hoffer et al., 2006), aldol condensation products (Noziere and Esteve, 2005, 2007), and nitrogen-containing compounds formed by the reaction of atmospheric aldehydes with ammonia or amines, e.g. imidazoles (Galloway et al., 2009; Lin et al., 2015b; Yu et al., 2011). Nitrated aromatic compounds (NACs), which are the focus of the present study, comprise another group of major contributors to BrC (Jacobson, 1999; Mohr et al., 2013). Nitrophenols (NPs) can be either emitted directly into the atmosphere, e.g. by traffic exhaust (Nojima et al., 1983; Tremp et al., 1993) and wood burning (Hoffmann et al., 2007) or secondarily formed by the nitration of precursor compounds like phenol either in the gas phase or liquid phase (Bolzacchini et al., 2001; Vione et al., 2002). [Nitrophenols-NPs](#) have been quantified at many different locations, especially in Europe (Cecinato et al., 2005; Iinuma et al., 2010; Kahnt et al., 2013; Zhang et al., 2010), but there is surprisingly little information on NP concentrations in Asia (Chow et al., 2015). Nitrated salicylic acids (NSAs) have also been recently detected in atmospheric aerosol particles (Kitanovski et al., 2012; van Pinxteren and Herrmann, 2007). A strong correlation with nitrate was found by Kitanovski et al. (2012) in samples from Ljubljana, Slovenia, suggesting secondary formation from precursor compounds such as salicylic acid, which has been found in biomass-burning aerosols as a lignin degradation product (Iinuma et al., 2007).

Studying BrC at a molecular level is considered important, since even trace levels of a compound could have a significant impact on the light absorption properties of particles (Kampf et al., 2012). However, little is known about the contributions of specific light absorbing compounds to the light absorption of either ambient aerosols or aqueous extracts from ambient particles.

Mohr et al. (2013) estimated the relative contribution of NACs to particulate BrC light absorption to be about 4 % at 370 nm at a measurement site in the United Kingdom with high influence of BB aerosols. Zhang et al. (2013) calculated a contribution of NACs to aqueous extract light absorption of 4 % from the Los Angeles basin (USA).

The present study aims to expand the understanding of BrC and water-soluble BrC by investigating its spatial and temporal variation in different, very diverse environments (urban, rural, biogenic, high BB influence). ~~Furthermore, including the contributions of individual light-absorbing organic compounds to the BrC light absorption is included.~~

2. Experimental

2.1 Measurement campaigns

Measurements took place at five sampling sites (three German and two Chinese), in six different atmospheric conditions. An overview over the sites, sampling periods, geographical coordinates, and the type of atmospheric environment is given in Table 1. Average temperatures and wind speeds are given as campaign averages.

The Leibniz Institute for Tropospheric Research (TROPOS (winter) campaign, 2014) is located in Leipzig in eastern Germany and can be regarded as a moderately polluted urban background site impacted by a mixture of ~~distributed various~~ sources (van Pinxteren et al., 2016). During the measurement period this site was strongly influenced by BB aerosols, as indicated by high levoglucosan concentrations. The first half of the campaign (~~24 until~~ 31 January) was characterized by low 12 h mean temperatures ≤ 0 °C. Afterwards, the temperature gradually increased towards the end of the campaign (up to 10 °C as 12 h mean). The periods of lower temperatures often coincided with increased emissions from residential heating. The average wind speed was 2.2 m s⁻¹.

The measurement site Waldstein in the Bavarian Fichtel Mountains (Waldstein (summer) campaign, 2014, Plewka et al. (2006)) is located about 180 km south west of Leipzig in a low mountain range. The site is surrounded by forest, where spruce is the dominant species. Measurements took place on a tower at a height of 21 m (about 780 m above sea level). The measurement period was characterized by low wind speeds (< 1.3 m s⁻¹) and predominantly sunny weather (average temperature of 19 °C).

Because of the surrounding forest, the influence of freshly emitted biogenic organics is expected to be high.

Measurements at Melpitz, a rural background site, located about 50 km north east of Leipzig, were carried out in winter (Melpitz (winter) campaign, 2014) and summer (Melpitz (summer) campaign, 2014). The Melpitz (winter) campaign was characterized by an average temperature of -3 °C and an average wind speed of 2.8 m s⁻¹. The Melpitz (summer) campaign was characterized by an average temperature of 22 °C and a mean wind speed of 2.0 m s⁻¹. The dates in winter and summer correspond to the measurement periods of the TROPOS (winter) and Waldstein (summer) campaigns, respectively. Due to the proximity of TROPOS and Melpitz, the two sites are influenced by similar regional air masses.

The Chinese measurement sites Xianghe (Xianghe (summer) campaign, 2013) and Wangdu (Wangdu (summer) campaign, 2014) are both located in the Hebei Province in the North China Plain (NCP). The campaigns were part of the CAREBeijing-NCP campaigns in 2013 and 2014. Xianghe is situated between the two megacities of Beijing and Tianjin, and Wangdu is located 170 km south west of Beijing. The average temperature and wind speed at the Xianghe (summer) campaign were 26 °C and 0.8 m s⁻¹, respectively. For the Wangdu (summer) campaign a mean temperature of 26 °C and a mean wind speed of 4 m s⁻¹ was measured. Both sites can be regarded as regional background stations for the NCP. In comparison to the summer campaigns in Germany, the average PM₁₀ (particulate matter with an aerodynamic diameter ≤ 10 μm) concentrations were about three to seven times higher at the Chinese sites.

2.1.2 Sampling, chemical analysis and back trajectories

~~Overall, eight NACs were determined as part of BrC: 3-nitrosalicylic acid (3NSA) and 5-nitrosalicylic acid (5NSA), 4-nitrophenol (4NP), 2-methyl-4-nitrophenol (2M4NP), 3-methyl-4-nitrophenol (3M4NP), 2,6-dimethyl-4-nitrophenol (2,6DM4NP), 2,4-dinitrophenol (24DNP) and 3,4-dinitrophenol (34DNP). The standard compounds were purchased in high purity ($\geq 98\%$) from either Fluka or Sigma-Aldrich (Munich, Germany).~~

~~PM₁₀ was collected on quartz fiber filters with a Digital 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~~

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5 samples (11 h or 12 h, see Table S1) were taken during each campaign except for Melpitz (winter) and Melpitz (summer), where particles were collected for 24 h. Details on the sampling times are given in Table S1. 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. Analysis of WSOC, levoglucosan, NACs and ~~the determination of~~ UV/Vis ~~spectrophotometry measurements spectra~~ were carried out using aqueous filter extracts of different portions of filter in ultrapure water. Details on the different methods are given below. The aqueous filter extract was always filtered through a pre-cleaned syringe filter (0.45µm, Acrodisc 13, Pall, Dreieich, Germany).

10 ~~Nitrated aromatic compound~~ NACs and UV/Vis spectra were determined from the aqueous extract by extracting 11–28 pieces of the filter (1.54 cm² each) into 10 mL of ultrapure water. ~~Nitrophenols~~ were analyzed according to the method described in Teich et al. (2014) based on hollow fiber liquid–phase micro extraction for analyte enrichment and capillary electrophoresis electrospray ionization mass spectrometry (CE-ESI-MS, Agilent ^{3D}CE instrument, Bruker Esquire 3000⁺ ion trap mass spectrometer). Samples from the Waldstein (summer) campaign were not analyzed for NPs, due to the limited availability of filter material.

15 ~~Nitrated salicylic acid~~ NSAs were enriched by evaporating an alkalized aliquot of the aqueous filter extract (1.8 mL plus 200 µL 10 mM NaOH) to dryness in a vacuum concentrator (miVac, Genevac Ltd., UK) and redissolving the residue into 40 µL ultrapure water. Subsequent analysis was carried out by CE-MS as described in van Pinxteren et al. (2012). Standard addition was carried out for quantifying the NSA compounds by co-injecting a standard solution plug at different concentration levels into the CE capillary after the sample plug.

20 Overall, eight NACs were determined as part of BrC: 3-nitrosalicylic acid (3NSA) and 5-nitrosalicylic acid (5NSA), 4-nitrophenol (4NP), 2-methyl-4-nitrophenol (2M4NP), 3-methyl-4-nitrophenol (3M4NP), 2,6-dimethyl-4-nitrophenol (2,6DM4NP), 2,4-dinitrophenol (24DNP) and 3,4-dinitrophenol (34DNP). The standard compounds were purchased in high purity (>98%) from either Fluka or Sigma–Aldrich (Munich, Germany).

25 As a typical BB tracer, levoglucosan can help to investigate the influence of BB aerosols on the observed concentrations (Iinuma et al., 2009; Simoneit, 2002). Levoglucosan was analyzed with a Dionex ICS-3000 system coupled with a pulsed amperometric detector (Thermo Fisher Scientific, Sunnyvale, CA, USA). A portion of sampled filter (9.42 cm²) was extracted in 20 mL of ultrapure water by shaking with a laboratory orbital shaker for 120 min. Detailed chromatographic conditions and the merits of analysis can be found elsewhere (Iinuma et al., 2009). Levoglucosan data is available for the campaigns Xianghe (summer), Wangdu (summer) and TROPOS (winter). No data is available for the Melpitz (winter), Melpitz (summer) and Waldstein (summer) campaigns, due to limited amount of filter material.

30 ~~Organic carbon~~ OC and elemental carbon (EC) were determined from the filter by a thermal-optical method using the Sunset Laboratory Dual-Optical Carbonaceous Analyzer (Sunset Laboratory Inc., Tigard, OR, USA) following the EUSAAR 2 temperature-protocol and applying a charring correction using light transmission (Cavalli et al., 2010).

35 The aqueous extract for determining WSOC was prepared by extracting 21.5 cm² of the filter samples from the Xianghe (summer), Wangdu (summer), Melpitz (winter) and Melpitz (summer) campaign and 38.5 cm² for samples from the campaigns Waldstein (summer) and TROPOS (winter) into 25 mL and 30 mL of ultrapure water, respectively, followed by 20 min of ultrasonication. After filtration, the extract was injected into a TOC-V_{CPH} analyzer (Shimadzu, Japan) operating in the NPOC (nonpurgeable organic carbon) mode. More details on the method can be found in van Pinxteren et al. (2009).

The air mass origin was estimated by 96 h back trajectories calculated using the HYSPLIT model (Draxler and Rolph, 2003).

2.23 Instrumentation for aerosol light absorption measurements

40 Particulate light absorption was measured by a seven–wavelength Aethalometer, model AE33 (Aerosol d.o.o., Slovenia) during the TROPOS (winter) and Waldstein (summer) campaigns. A detailed description of the instrument is given in Drinovec et al. (2015). Briefly, aerosol particles are collected on a filter tape. Light attenuation is measured continuously through this aerosol

laden filter (time resolution of 1s). When a fixed attenuation threshold is reached, the tape advances to a new filter spot. Filter-based measurements feature non-linear loading effects, caused by the increasing deposition of the sample in the filter loading during the measurement, and filter matrix light scattering effects (Weingartner et al., 2003). The Aethalometer AE33 measures the loading effect by using a dual-spot approach, where attenuation measurements are carried out simultaneously on two differently loaded spots. Multiple scattering effects were compensated by normalizing the particulate light absorption coefficient b_{abs} against data from a Multi-Angle Absorption Photometer (MAAP, Petzold and Schonlinner (2004)) which was also located at the measurement sites. The determined normalization factor (for light scattering effects) C was 1.69 for the TROPOS (winter) campaign and 2.06 for the Waldstein (summer) campaign. More details are given in the supplement Sect. S1.

The relative contribution of BrC and BC to $b_{\text{abs},370}$ was determined following the method used by Kirchstetter and Thatcher (2012). For the calculations, it was assumed that BC was the only absorbing species at 940 nm, OC and BC were externally mixed, and that the AAE of BC was 1.0. These assumptions are consistent with recently published studies (Martinsson et al., 2015; Mohr et al., 2013). Using Eq. (1), $b_{\text{abs},370,\text{BC}}$ was determined by extrapolating from 940 nm to 370 nm, and the contribution of BrC was then calculated using Eq (2):

$$b_{\text{abs},\lambda} = b_{\text{abs},\lambda,\text{BrC}} + b_{\text{abs},\lambda,\text{BC}} \quad (2)$$

The AAE was fitted over all seven wavelength and is given as the average of the wavelength dependencies with the measurement time resolution.

2.4.3 UV/Vis spectrophotometry

Light absorption of aqueous solutions were measured with a Lambda 900 UV/Vis-spectrophotometer (Perkin Elmer) using quartz cells (Secomam, France). The aqueous filter extracts were analyzed at pH≈2 (acidified with H₂SO₄, in the following also indicated with the subscript “A”) and at pH≈10 (addition of NaOH, in the following also indicated with the subscript “B”). Hence, the target compounds were either in their neutral or deprotonated state 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 were kept in the dark and analyzed as soon as possible after preparation by UV-Vis-spectrophotometry. The influence of the pH on MAE and the aqueous light absorption coefficient (Abs) is discussed in Sect. 3.1.1. Spectra were recorded from 300 to 800 nm.

The interpretation of the aqueous extract light absorption follows the method described by Hecobian et al. (2010). In general, according to Beer–Lambert–Law the absorbance (A_λ) of a solution is defined as:

$$A_\lambda = -\log_{10}\left(\frac{I}{I_0}\right) = l \cdot c \cdot \varepsilon_\lambda = l \sum_i (c_i \cdot \varepsilon_{\lambda,i}), \quad (3)$$

where I_0 and I are the intensity of the incident and transmitted light, respectively, l the absorbing path length, c the concentration of absorbing species in solution and ε_i is the wavelength dependent molar extinction coefficient. The resulting data was then converted to the aqueous light absorption coefficient Abs_λ .

$$\text{Abs}_\lambda [\text{Mm}^{-1}] = (A_\lambda - A_{800}) \frac{V_l}{V_a l} \cdot \ln(10), \quad (4)$$

where A_{800} is the reference wavelength to account for any baseline drift, V_l is the volume of water used for extraction (10 mL), V_a is the volume of air passed through the filter, and $\ln(10)$ was used to convert the common logarithm to a natural logarithm. The path length l was either 2 or 5 cm.

Abs_λ is the light absorption coefficient of the aqueous extract solutions and is not to be mistaken for b_{abs} , the light absorption coefficient of ambient particles. This nomenclature was chosen in accordance with other studies (Liu et al., 2013a, 2015).

Using the mass concentration of WSOC (in $\mu\text{g m}^{-3}$), MAE was calculated by:

$$MAE[m^2g^{-1}] = \frac{Abs_{\lambda}}{[WSOC]} \quad (5)$$

The molar extinction coefficient at 370 nm, ϵ_{370} , was determined for each target compound by preparing a dilution series of standard compounds in water. Subsequently, a three point curve was recorded twice. According to the Beer–Lambert–Law, the slope of the regression in an absorbance–concentration–plot is proportional to ϵ . The molar extinction coefficients for each compound under acidic and alkaline conditions are presented in Table S23.

In other studies dealing with aqueous extracts, Abs values were given for 365 nm (e.g., Bosch et al., 2014; Cheng et al., 2011; Hecobian et al., 2010). We chose 370 nm to characterize the aqueous extract light absorption properties to match the 370 nm channel of the Aethalometer.

2.5.4 Calculation of the contribution of nitrated aromatic compounds to light absorption of aqueous extracts and particulate brown carbon

The contribution of the target compounds to the aqueous extract light absorption was computed by first calculating the absorbance of the single compound using Eq. (3) and then determining the percentage on the total aqueous solution light absorption.

To assess the contribution of the NACs to particulate BrC light absorption at 370 nm, the molar extinction coefficient of each compound was converted to the liquid phase molecular absorption cross section b_{liq} (Jacobson, 1999):

$$b_{liq}[cm^2molecule^{-1}] = 1000 \ln(10) \frac{\epsilon_{370}}{N_A} \quad (6)$$

where N_A is the Avogadro constant and $\ln(10)$ is used to convert the common logarithm of the molar extinction coefficient (base 10) to the natural logarithm. The MAE_{comp} of each compound was then calculated by dividing b_{liq} by the mass of one molecule. The subscript “comp” denotes the specific compound. If the MAE_{comp} and the mass concentration in air of the compound are known, $b_{abs,comp}$ of the single compound in ambient particles can be calculated by the following equation:

$$b_{abs,comp} = MAE_{com} \cdot [comp] \quad (7)$$

where $[comp]$ is the mass concentration of the compound in the aerosol.

By knowing $b_{abs,comp}$ and $b_{abs,BrC}$, the relative contribution of the individual compound on the particulate BrC light absorption can be calculated.

3. Results/Discussion

3.1. Optical properties of water-soluble and particulate brown carbon

In the following section, the general optical properties of water-soluble and particulate BrC are presented. Optical properties of water-soluble BrC (represented by the aqueous extract light absorption) are given as MAE_{370} and the aqueous light absorption coefficient (Abs_{370}). Particulate BrC was characterized by the particulate light absorption coefficient ($b_{abs,370}$) and the AAE. The results of the optical properties are summarized in Table 2.

3.1.1 Influence of acidic and alkaline conditions on the mass absorption efficiency and the aqueous light absorption coefficient

Values for MAE and Abs have usually been directly derived from filtered aqueous filter extract without considering the pH of the solutions (e.g., Bosch et al., 2014; Cheng et al., 2011; Hecobian et al., 2010). However, depending on the nature of the absorbing species, pH alters the absorptivity. Alif et al. (1987,1990,1991) showed for NPs that their anionic form is a much stronger absorber than their neutral form. Moreover, the absorption maximum shifts towards longer wavelengths under alkaline conditions. The dissociation in a solution depends on the pK_a value of the compound and at different pH levels different mixtures of neutral/ionized compounds exist. Generally, ambient particles are estimated to be more acidic (pH<4, Scheinhardt

et al., 2013), making the findings under acidic conditions more relevant for ambient conditions. However, Hinrichs et al. (2016) reported, that NPs adsorbed to a particle surface exhibit a significant red-shift similar to the aqueous light absorption spectrum of their deprotonated form. Hence, under certain conditions the deprotonated forms can also be important.

Comparing alkaline and acidic conditions, strong correlations have been found for Abs, MAE and the relative contribution of the individual compounds to Abs over all campaigns ($R^2 \geq 0.93$, see Fig. S3). On average, Abs₃₇₀ increased by a factor of 1.4 and MAE by a factor of 1.6 under alkaline conditions compared to the acidic conditions. As indicated by the good correlation, this factor is quite consistent and independent of the measurement site.

The molar extinction coefficient at 370 nm increases with pH for the individual compounds (see Table S23). A higher pH leads to deprotonation of hydroxyl and carboxyl groups, which may lead to a shift of the absorption maximum towards longer wavelengths. The light absorption of the aqueous extracts is a sum of many different light absorbing species. Therefore, the relative contribution to the aqueous extract light absorption for individual compounds is affected differently. For example, the relative contribution of 3NSA and 2,6DM4NP to Abs₃₇₀ decreases at pH 10. No difference in the contribution to Abs₃₇₀ was observed for 5NSA. The highest increase in the contribution to Abs₃₇₀ was found for 2,4DNP with a factor of 6.8. The observed differences in the contribution to Abs₃₇₀ are related to both the molar extinction coefficient, which alters with the pH, and the composition of the solution. A decrease in the relative contribution to the light absorption at higher pH is most likely due to greater contributions of other, now overlapping light absorbing compounds at this specific wavelength.

The increase of Abs₃₇₀ with higher pH is relatively modest (a factor of 1.4) compared to the increase of the molar extinction coefficient of individual NACs (an average factor of 4.5). This might indicate that the absorption properties of the majority of light absorbing compounds are little affected by the pH. These findings are only valid for the investigated wavelength of 370 nm and are likely to differ over the whole spectral range.

Due to the close relationship between MAE and Abs under alkaline and acidic conditions, only the values for the acidic conditions are discussed in the following section (Sect. 3.1.2), while both of them are always displayed in the Figures and Tables.

3.1.2. Mass absorption efficiency and aqueous light absorption coefficient of water-soluble brown carbon

The temporal evolution of Abs₃₇₀ and MAE_{370A} for each measurement site are shown in Fig. 1. The highest mean MAE_{370A} values were found for the campaigns Melpitz (winter, $0.86 \pm 0.33 \text{ m}^2 \text{ g}^{-1}$) and TROPOS (winter, $0.84 \pm 0.20 \text{ m}^2 \text{ g}^{-1}$) followed by Wangdu (summer, $0.55 \pm 0.15 \text{ m}^2 \text{ g}^{-1}$) and Xianghe (summer, $0.38 \pm 0.06 \text{ m}^2 \text{ g}^{-1}$). The lowest values were observed under summer conditions in Germany, where the values for the Melpitz (summer) campaign slightly exceeded the MAE_{370A} observed at the Waldstein (summer) campaign ($0.22 \pm 0.03 \text{ m}^2 \text{ g}^{-1}$ over $0.17 \pm 0.03 \text{ m}^2 \text{ g}^{-1}$). Measured MAE_{370A} values for China are in the same range or slightly lower than values reported in other studies. For instance, several studies were conducted in Beijing in summer, where Cheng et al. (2011) determined an average MAE of $0.7 \text{ m}^2 \text{ g}^{-1}$, Du et al. (2014) found $0.5 \text{ m}^2 \text{ g}^{-1}$ and Yan et al. (2015) observed $0.7 \text{ m}^2 \text{ g}^{-1}$ (all values determined at 365 nm). The findings for the TROPOS (winter) and Melpitz (winter) campaigns suggest regional behavior and are comparable to observed MAEs from urban sites in the US (Hecobian et al. (2010), $0.47\text{-}0.87 \text{ m}^2 \text{ g}^{-1}$, annual mean, determined at 365 nm). Low MAE values, similar to the observed MAEs at the Melpitz (summer) and Waldstein (summer) campaigns, have been found at urban and rural sites in the U.S. (0.21 and $0.12 \text{ m}^2 \text{ g}^{-1}$, respectively, determined at 365 nm) when the concentration of levoglucosan was low ($<50 \text{ ng m}^{-3}$). Although the average Abs_{370A} is similar for the campaigns of Wangdu (summer), TROPOS (winter) and Melpitz (winter) (4.64 , 3.92 and 4.13 Mm^{-1} , respectively), the observed mean MAE_{370A} for the Wangdu (summer) campaign is lower, indicating that despite higher concentrations of OC and WSOC during the Wangdu (summer) campaign (see Table S34), fewer light absorbing compounds were present.

A correlation between levoglucosan and Abs₃₇₀ was found during the TROPOS (winter) campaign ($R^2 = 0.8$), and during the BB episode of the Wangdu (summer) campaign ($R^2 = 0.9$), when BB aerosol was abundant (see Fig. 2). This correlation suggests that BB aerosol is a major contributor to the aqueous extract light absorption. The connection between BB and light

absorbing BrC was also observed in a number of other studies (e.g., Desyaterik et al., 2013; Hoffer et al., 2006; Lack et al., 2013; Mohr et al., 2013). During non-BB episodes of the Wangdu (summer) campaign and the Xianghe (summer) campaign, only a weak or no correlation at all was observed between levoglucosan and Abs_{370} (see Fig. 2). This indicates the presence of sources for light absorbing compounds other than BB aerosols. A decay of levoglucosan more rapid than the decay of NACs might also be a cause for this observation (Hoffmann et al., 2010).

Regarding seasonal differences, the aqueous extract light absorption was much lower in summer compared to winter samples. This is a general trend, observed at many measurement sites (e.g., Du et al., 2014; Hecobian et al., 2010; Kim et al., 2016). Kim et al. (2016) suggested that this is either because the amount of emitted BrC is much higher during winter or that summer BrC is less water-soluble. By comparing aqueous extract light absorption to ambient particle light absorption measurements this issue will be further explored and discussed in the following section.

3.1.3 Particulate light absorption coefficient and absorption Ångström exponent of particulate brown carbon

The temporal evolution of the measured particulate light absorption coefficient b_{abs} at 370 nm as well as the determined contributions of particulate BrC and BC to the light absorption at 370 nm are shown in Fig. 3. Normalizing the determined b_{abs} for particulate BrC by the according OC content gives the mass absorption efficiency for BrC in the particle ($MAE_{370, BrC, particle}$). The temporal variation of $MAE_{370, BrC, particle}$ is displayed in Fig. S4. The AAE (as campaign average) obtained by fitting over all Aethalometer wavelengths was 1.5 ± 0.1 and 1.2 ± 0.3 for the campaigns TROPOS (winter) and Waldstein (summer), respectively. An AAE close to one indicates that BC is the dominant species (Kirchstetter et al., 2004). The increased AAE values indicate that BrC plays a larger role for the TROPOS (winter) campaign than for the Waldstein (summer) campaign, where its contribution is minor.

During the BB influenced TROPOS (winter) campaign, the mean total $b_{abs,370}$ was 54 Mm^{-1} . Particulate BrC contributed about 40 % to the overall light absorption at 370 nm and an average $MAE_{370, BrC, particle}$ of $1.95 \text{ m}^2 \text{ g}^{-1}$ was calculated. The influence of BB on the light absorption of ambient particles has also been observed in other studies. For instance, Kirchstetter and Thatcher (2012) estimated that the contribution of BrC to the light absorption of wood smoke is 49 % below 400 nm from samples collected in wintertime California (U.S.). Mohr et al. (2013) found a BrC contribution of 46 % to $b_{abs,370}$ at a UK site that was highly influenced by BB. Our findings on the contribution of BrC to $b_{abs,370}$ during the TROPOS (winter) campaign are consistent with these earlier measurements. The light absorption was observed to be higher for easterly air masses than those from the west, a trend also seen in the NAC concentrations of the TROPOS (winter) campaign (see Sect. 3.2). Easterly winds were often accompanied by lower temperatures or thermal inversion layers or both. Therefore, higher concentrations of light absorbing compounds (and higher particulate light absorption) might be a result of both, increased emissions (locally and in the source region) and lower dispersion of absorbing pollutants due to the thermal inversion layer.

In contrast, the light absorption of aerosol particles -was much lower during the Waldstein (summer) campaign with a mean total $b_{abs,370}$ of 6 Mm^{-1} , a $MAE_{370, BrC, particle}$ of $0.21 \text{ m}^2 \text{ g}^{-1}$ and a BrC contribution to the particulate light absorption of about 15 % at 370 nm. The measurements at Waldstein (which is surrounded by a mixed forest) were carried out in a sunny summer period when high biogenic emissions would strongly influence the results. Several laboratory studies have shown that the formation of light absorbing compounds from biogenic precursors is negligible (e.g., Liu et al., 2013b; Nakayama et al., 2010; Song et al., 2013). However, a few studies have suggested that BrC might be formed in the presence of high ammonia concentrations (Flores et al., 2014; Updyke et al., 2012) or from isoprene epoxydiols (IEPOX, Lin et al., 2014). Findings from field measurements in the Amazon Basin confirmed that the light absorption by biogenic aerosol is much lower than the light absorption of BB aerosols or BC (Rizzo et al., 2011). Compared to the TROPOS (winter) campaign, b_{abs} for BrC is very small for the Waldstein (summer) campaign, with an average of 0.94 Mm^{-1} compared to 21.8 Mm^{-1} . Our findings corroborate those of Rizzo et al. (2011) and laboratory studies stating that biogenic aerosols alone produce only small amounts of light absorbing compounds.

The relative contribution of light-absorbing WSOC to particulate light absorption can be estimated by applying a conversion factor. Based on Mie theory calculations, Liu et al. (2013a) suggested a factor of two to convert the aqueous extract light absorption coefficient (Abs) into the particulate light absorption coefficient (b_{abs}). The temporal variation of the fraction of the converted Abs₃₇₀ to the particulate BrC light absorption is given in Fig. S4. For our data, ~~this gives~~ a good agreement between the Waldstein (summer) average Abs_{370A} (0.51 Mm⁻¹ x 2) and the Waldstein (summer) average $b_{\text{abs},370,\text{BrC}}$ (0.94 Mm⁻¹) was achieved, suggesting that the observed particulate light absorption is mainly associated with water-soluble compounds during this campaign. For the TROPOS (winter) campaign, doubling the average Abs_{370A} gives a value of 7.8 Mm⁻¹, which is still much lower than the average $b_{\text{abs},370,\text{BrC}}$ (21.8 Mm⁻¹). Thus, a large fraction of non-water-soluble OC likely exists as well, that is highly light absorbing at 370 nm.

3.2. Concentrations of nitrated aromatic compounds under different atmospheric conditions

This section presents an overview and a comparison of the NAC concentrations for all campaigns. Table 3 summarizes the measured concentrations in comparison with other studies at similar locations. The results of the temporal variation of the target compounds for each campaign are displayed in Fig. 1.

A general concentration trend of 4NP > 3M4NP > 2M4NP > 2,6DM4NP > 2,4DNP > 3,4DNP and 3NSA > 5NSA was observed for all campaigns of the present study and is in good agreement with findings from most other studies. Regarding the sum of NPs, the mean concentrations were highest during the TROPOS (winter) campaign (14.0 ng m⁻³) followed by the Melpitz (winter) campaign (11.1 ng m⁻³). These concentrations are a factor of 3 to 10 higher than those observed during the campaigns Wangdu (summer) and Xianghe (summer) (4.4 ng m⁻³ and 1.4 ng m⁻³, respectively). During the Melpitz (summer) campaign, the NP concentration was 100 times lower (average of 0.1 ng m⁻³) than during the Melpitz (winter) campaign. For the sum of NSAs, the highest mean concentrations were found at the Wangdu (summer) campaign (4.8 ng m⁻³) followed by the campaigns Xianghe (summer) and TROPOS (winter) (average of 2.2 ng m⁻³, each). Average concentrations for NSAs of ≤ 1 ng m⁻³ were observed at the campaigns Melpitz (winter, 1.0 ng m⁻³), Waldstein (summer, 0.4 ng m⁻³) and Melpitz (summer, 0.2 ng m⁻³).

A clear seasonality can be seen in the data from the German sites. The observed concentrations of the different species are generally lower in summer than in winter because the sources of NACs are stronger during winter and generally connected to polluted air, as discussed in the Sect. 1.

The campaigns Melpitz (winter) and TROPOS (winter) were carried out in the same period and the two sites are directly comparable due to their geographic proximity. Concentrations of the NACs are in the same range at both sites and show a common pattern. Two periods with concentration maxima were found. The first period occurred around 25 January and the second peak was around 30 January, 2014 (see Fig. 1, a and b). Both periods are characterized by prevailing easterly winds and shorter mean lengths of 96-hour back trajectories. In contrast, air masses during other periods originated from the south west and had longer trajectories and increased residence times over the Atlantic Ocean. Higher concentrations of PM and many of its constituents with easterly winds are often observed at Melpitz (Spindler et al., 2010). The long residence time above the continent results in increased concentrations of pollutants in those air masses. Furthermore, as described in Sect. 3.1.3, the temperature was generally lower when the air mass originated from the east, which likely led to higher emissions from residential heating both locally and in the air mass source regions.

The campaigns Melpitz (summer) and Waldstein (summer) were also conducted in the same time period. The concentrations of NSAs are comparable at both sites (0.01-0.51 ng m⁻³) and are very low compared to the winter measurements. NPNitrophenols were not analysed from the Waldstein (summer) campaign as explained above.

Day and night samples were collected during the campaigns TROPOS (winter), Waldstein (summer), Xianghe (summer) and Wangdu (summer). Nighttime concentrations of the sum of NACs were found to be slightly higher than during the day (not statistically significant at 95 % confidence level). The lower daytime concentrations are probably caused by the higher

boundary layer heights during the day, i.e. dilution effects, and/or lower emission/formations rates during daytime or photolysis processes.

The sum of all target compounds at the TROPOS (winter) campaign was only weakly correlated with levoglucosan ($R^2 = 0.47$, Fig. S45), indicating that BB was not the dominant source of NACs during the campaign. As mentioned above, the formation or decay processes of levoglucosan and NACs might be very different, which resulted in no correlation of those species. It is also known, that the sources of NACs are very diverse (see Sect. 1).

At the Wangdu (summer) campaign, a BB episode was observed between 11 June and 19 June (see Fig. 1f), indicated by a peak in measured levoglucosan concentrations. During that period, increased concentrations of NACs were found. Although the NAC concentration generally increased with increasing levoglucosan concentration, no clear connection between NACs and BB aerosols was found. For the Xianghe (summer) campaign, levoglucosan concentrations (average of 109 ng m^{-3}) were lower than for the Wangdu (summer) or TROPOS (winter) campaign, suggesting that BB played a minor role at this site during the time of measurements. No correlation was found between the sum of NACs and levoglucosan. This implies that BB was neither the major source of NACs in the Wangdu (summer) nor in the Xianghe (summer) campaign. 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.

Nitrated aromatic compoundsNACs seem to be ubiquitous and are found at each site in measurable amounts although they are highly variable at the different measurement sites. The sum of NAC concentrations at the different campaigns followed the order TROPOS (winter) > Melpitz (winter) > Wangdu (summer) > Xianghe (summer) > Waldstein (summer) > Melpitz (summer). This trend might be considered surprising, since the average PM_{10} and OC values were higher at the Chinese sites than at the German sites (see Table S34). However, the seasonality and influence of BB aerosol seems to play a large role for the NAC concentration resulting in lower concentrations at the Chinese summer sites than at the German winter sites.

3.3. Contribution of nitrated aromatic compounds to water-soluble and particulate brown carbon

In this section, the contribution of NACs to the aqueous extract light absorption and then the contribution of NACs to the particulate BrC light absorption are discussed. The relative contribution of NACs to Abs_{370} is shown in Fig. 4 together with the contribution of NACs to the WSOC concentration. Table 2 summarizes the contribution of NSAs and NPs to aqueous extract light absorption (Abs) and particulate BrC light absorption (b_{abs}). The focus is on the relative contribution to the aqueous extract light absorption at the wavelength of 370 nm to match the 370 nm channel of the Aethalometer. To give additional information, the relative contribution of NACs to Abs (acidic conditions) over a spectral range of 300 to 500 nm is presented in Fig. 5 as their campaign averages.

The relative NAC contribution to aqueous extract light absorption Abs_{370} varied greatly across the different sites, ranging from 0.02 to 4.41 % for acidic conditions and from 0.02 to 9.86 % for alkaline conditions. This result likely reflects the dependence of NAC source strength on location and seasonality. The maximum contribution of NACs to Abs_{370} was found for the TROPOS (winter) campaign. The contribution of NACs to Abs_{370} was low for the campaigns Waldstein (summer) and Melpitz (summer). For the Waldstein (summer) campaign, a mean contribution of 0.15 % (acidic) or 0.13 % (alkaline) was observed. Average values of 0.13 % (acidic) and 0.24 % (alkaline) were obtained from the Melpitz (summer) campaign. 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. The results for the Xianghe (summer) and Wangdu (summer) campaigns are about half the values of the TROPOS (winter) or Melpitz (winter) campaigns. This shows, that NACs in the present study had a much higher impact on the light absorption properties

during the German winter campaigns than during the Chinese summer campaigns and indicates that other compounds play a larger role in particle light absorption at the Chinese sites. More studies are needed to resolve the molecular identity and abundance of these light absorbing compounds.

The relative contribution of NACs to Abs is wavelength dependent. Under acidic conditions, the contribution of NACs to the aqueous extract light absorption increases towards lower wavelength, reaching a maximum that was found to generally lie in the range of 330 - 350 nm (see Fig. 5). Moreover, it can be seen that maximum values differ for individual compounds. Under alkaline conditions, this maximum shifts towards the range of 400 - 420 nm (see Fig. S6). As stated above, the results for acidic conditions are likely to be more atmospherically relevant. Therefore, a higher influence of NACs towards shorter wavelengths suggests that they can be more important in terms of their influence on atmospheric photochemistry, e.g. O₃ photolysis (Jacobson, 1999).

The relative mass contribution of NACs to the WSOC concentration at the different campaigns follows the same pattern as the contribution of NACs to the aqueous extract light absorption and also the same pattern as the NAC concentrations (see Sect. 3.2 and Fig. 4). The highest mass contributions of NACs were found during the TROPOS (winter) campaign followed by the Melpitz (winter) campaign, and lowest values were observed for the campaigns Waldstein (summer) and Melpitz (summer).

The average mass contribution of NACs to WSOC is less than 0.2% at each site. In contrast, NACs have a mean contribution to aqueous extract light absorption of 1%, which is a factor of five larger than their mass contribution to WSOC. Our results corroborate the findings of other studies, which show that even small amounts of light absorbing compounds can significantly impact the light absorption properties of particles. As a result, a detailed investigation of the molecular composition of BrC is important (Kampf et al., 2012; Laskin et al., 2015).

The correlation between NAC concentrations and Abs₃₇₀ for each campaign is displayed in Fig. 56. The correlation is good for the TROPOS (winter) and Melpitz (winter) campaign ($R^2=0.7$, each) and weaker for the Wangdu (summer) campaign ($R^2=0.6$). No correlation was found for the campaigns Xianghe (summer), Melpitz (summer) and Waldstein (summer). In general, the presence of high NAC concentrations also indicates higher values for Abs₃₇₀ than at sites with lower NAC concentrations. However, due to the diverse sources and sinks (e.g. photobleaching (Zhao et al., 2015)) of NACs and BrC, NACs cannot be considered as the only tracers for BrC for very different atmospheric conditions.

The average contribution of NACs to particulate BrC light absorption, was found to be 0.10% for the Waldstein (summer) campaign and 0.25% for the TROPOS (winter) campaign for the protonated forms, and 0.13% and 1.18%, respectively, for their deprotonated forms. The contribution during the Waldstein (summer) campaign is similar for the aqueous extract and aerosol light absorption, which is consistent with the assumption discussed above that the observed light absorption is mostly derived from WSOC and no further water-insoluble BrC was present at this site.

To the best of the author's knowledge, up to now only two other field studies have determined the contribution of individual compounds to BrC light absorption. Zhang et al. (2013) estimated the contribution of eight NACs to aqueous extract light absorption in Los Angeles to be about 4% at 365 nm, while Mohr et al. (2013) estimated a NAC contribution of 4% to particulate BrC light absorption at 370 nm at a BB influenced site in the U.K. The findings from Zhang et al. (2013) are in the same range as our findings for the TROPOS (winter) campaign (for Abs₃₇₀), whereas the estimated contribution of NACs to particulate BrC light absorption by Mohr et al. (2013) is a factor of 16 larger than our observed contributions. One possible reason for this discrepancy is that the mean $b_{\text{abs,BrC}}$ measured in the present study is about twice as high as observed by Mohr et al. (2013) (10 Mm^{-1}) while the concentrations of NACs are in the same range in both studies. Moreover, Mohr et al. (2013) considered a different suite of NACs than the present study. Another important point is that the calculation by Mohr et al. (2013) used values based on the absorption maxima of the individual species, which usually lie below 370 nm (for their protonated form). In contrast, in the present study the molar extinction coefficient of each compound was directly determined at 370 nm. When calculations were made based on the absorption maxima of protonated NACs, an average contribution to the particulate BrC light absorption of 1% was found for the present study, i.e. a factor of four higher than the calculation at 370

nm. This suggests that the influence of NACs is higher towards shorter wavelength, i.e. near their absorption maximum and thus can be more important in terms of their influence on atmospheric photochemistry, e.g. O₃ photolysis (Jacobson, 1999).

4. Conclusions

In the present study, the contributions of eight NACs to the light absorption of aqueous particle extracts and particulate BrC were determined in Germany and China at five measurement sites under six different atmospheric conditions.

The effect of pH on the aqueous extracts light absorption was investigated. Absorption of extracts at 370 nm, Abs₃₇₀, increased by a factor of 1.4 and MAE by a factor of 1.6 when the pH was increased from 2 to 10. A general seasonal trend of MAE₃₇₀ and Abs₃₇₀ being higher in winter than in summer was observed, which is in agreement with other studies. The MAE values during winter times impacted by BB in Germany exceeded those of the Chinese background stations during summer. Very low MAE and *b*_{abs,370} were observed at the forest site Waldstein in summer, indicating that freshly emitted biogenic aerosols are only weakly absorbing. In contrast, a strong relationship was found between the light absorption properties and BB aerosol concentrations, corroborating findings from other studies. An average contribution of particulate BrC to *b*_{abs,370} of 46% was observed during the TROPOS (winter) campaign and 15% during the Waldstein (summer) campaign. The AAE of particulate BrC was found to be 1.5 and 1.2 for the campaigns TROPOS (winter) and Waldstein (summer), respectively.

The relative contribution of NACs to the aqueous extract light absorption was highly variable depending on the measurement site, ranging from 0.02% to 4.41% under acidic conditions and 0.02% to 9.86% under alkaline conditions. This indicates that the emission strength of light absorbing compounds and the composition of BrC differed between the sites. In addition, the formation and decay processes might be very different in the respective environments. The mean contribution of NACs to the particulate BrC light absorption was 0.10% (acidic conditions) and 0.13% (alkaline conditions) during the Waldstein (summer) campaign and 0.23% (acidic conditions) and 1.15% (alkaline conditions) during the TROPOS (winter) campaign. A correlation between the NAC concentration and Abs₃₇₀ was observed during the campaigns TROPOS (winter) and Melpitz (winter), at other sites the correlation was weak or non-existent.

The mass contribution of NACs to WSOC was five times lower than their contribution to the aqueous extract light absorption. This corroborates conclusions of other studies that even small amounts of light absorbing compounds can have a disproportionately high impact on the aerosol light absorption properties (Kampf et al., 2012).

Field studies on the molecular composition of BrC are still scarce, especially for sites that have no or little influence of BB aerosols. Therefore, more efforts are needed to assess BrC on a molecular level, since a deeper knowledge of the present light absorbing compounds can improve the understanding and prediction of BrC aging processes and its radiative forcing (Laskin et al., 2015). A further investigation of BrC compounds may also result in finding tracer compounds for specific BrC sources.

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Table 1. Overview over sampling sites, used terminology, sampling period, sampling duration and according atmospheric conditions during the sampling period.

Sampling site	Designation	Geographic coordinates	Sampling period (sampling duration per filter)	Comments
Germany				
Roof of the Leibniz Institute for Tropospheric Research, Leipzig	TROPOS (winter)	51.35 °N, 12.43 °E	24 January to 08 February 2014 (12 h, day <u>06:00–18:00 LT</u> , and night <u>18:00–06:00 LT</u>)	Urban background, strong influence of biomass burning aerosol during measurement period (van Pinxteren et al., 2016)
Melpitz	Melpitz (winter)	51.53 °N, 12.93 °E	24 January to 04 February 2014 (24 h, <u>00:00–24:00 LT</u>)	Rural background (Spindler et al., 2010)
Melpitz	Melpitz (summer)		16 July 2014 to 25 July 2014 (24 h, <u>00:00–24:00 LT</u>)	
Bavarian Fichtel Mountains	Waldstein (summer)	50.14 °N, 11.87 °E	16 July to 25 July 2014 (11 h, day, <u>07:00–18:00 LT</u> , and night, <u>19:00–06:00 LT</u>)	BayCEER Waldstein observatory, F-BEACH campaign, surrounded by forest, high local biogenic emissions (Plewka et al., 2006)
China				
Xianghe	Xianghe (summer)	39.75 °N, 116.96 °E	09 July to 14 July and 21 July 2013 to 01 August 2013 (12 h, day, <u>06:00–18:00 LT</u> and night, <u>18:00–06:00 LT</u>)	CAREBeijing–NCP 2013 campaign (Kecorius et al., 2015), rural background, urban outflow
Wangdu	Wangdu (summer)	38.71 °N, 115.13 °E	04 June to 24 June 2014 (12 h, day, <u>06:00–18:00 LT</u> , and night, <u>18:00–06:00 LT</u>)	CAREBeijing–NCP 2014 campaign, rural background, biomass burning episode occurred during the measurement period (Kecorius et al., 2016)



Table 2. Optical properties and calculated contribution of NACs to the light absorption of aqueous extracts and particulate BrC. The values are given as: minimum-maximum (mean \pm standard deviation). **Acidic conditions are indicated by the letter "A," and alkaline conditions are indicated by the letter "B". Highest and lowest mean values for each category are marked in bold.**

	Waldstein (summer)	Melpitz (summer)	TROPOS (winter)	Melpitz (winter)	Xianghe (summer)	Wangdu (summer)
Optical properties						
Abs_{370A} [Mm⁻¹]	0.21-0.70 (0.51±0.11)	0.57-1.34 (0.84±0.24)	0.33-8.96 (3.91±2.49)	1.75-10.6 (4.13±2.51)	0.82-4.68 (2.02±0.81)	1.10-21.8 (4.64±4.16)
Abs_{370B} [Mm⁻¹]	0.63-1.15 (0.88±0.13)	0.88-1.78 (1.19±0.30)	0.69-14.5 (6.80±3.94)	3.28-15.2 (6.63±3.50)	1.20-9.07 (3.16±1.50)	1.87-27.2 (6.65±5.55)
MAE_{370A} [m² g⁻¹]	0.10-0.25 (0.17±0.03)	0.19-0.30 (0.22±0.03)	0.41-1.30 (0.84±0.20)	0.52-1.79 (0.86±0.33)	0.30-0.52 (0.38±0.06)	0.31-1.01 (0.55±0.15)
MAE_{370B} [m² g⁻¹]	0.24-0.36 (0.29±0.03)	0.27-0.43 (0.31±0.05)	0.86-2.21 (1.45±0.29)	0.84-2.57 (1.37±0.45)	0.34-1.15 (0.59±0.14)	0.49-1.40 (0.81±0.21)
b_{abs370} [Mm⁻¹]	3.72-8.59 (6.23±1.33)		4.13-129.4 (54.2±34.07)			
b_{abs370,OC} [Mm⁻¹]	0.62-1.69 (0.94±0.28)		1.25-54.4 (21.8±14.2)			
Contribution to light absorption [%]						
NACs_A to Abs_{370A}	0.02-0.33 (0.15±0.10)	0.063-0.2243 (0.1398±0.054)	0.037-32.40⁻⁴-4.220.19 (1.210.11±0.8296)	0.1591-2.030.19 (0.8706±0.5795)	0.042-1.3292 (0.4626±0.249)	0.2404-1.830.89 (0.5629±0.3119)
NSA-NACs to Abs_{370B}	0.02-0.25 (0.13±0.03)	0.1093-0.4813 (0.2407±0.1204)	0.975.9.10⁻⁴-9.710.15 (3.350.09±2.040.05)	0.47004-5.000.09 (2.480.05±1.450.03)	0.2101-2.850.81 (0.1.0222±0.0.5416)	0.5604-4.440.71 (1.340.25±0.7215)
NSA-NACs to b_{abs370,BrCOC} (A)	0.01-0.22 (0.10±0.06)		0.0101-1.130.04 (0.2502±0.2104)			
NSA-NACs to b_{abs370,BrCOC} (B)	0.02-0.31 (0.13±0.09)		0.001-5.420.06 (1.130.03±1.030.01)			
NP to Abs_{370A}		0.02-0.09 (0.05±0.02)	0.33-4.22 (1.14±0.82)	0.44-1.84 (0.81±0.52)	0.04-0.62 (0.22±0.13)	0.10-1.19 (0.26±0.17)
NP to Abs_{370B}		0.07-0.35 (0.17±0.09)	0.91-9.71 (3.62±2.05)	0.47-4.90 (2.43±1.42)	0.17-2.72 (0.83±0.53)	0.38-3.97 (1.02±0.59)
NP to b_{abs370,OC} (A)			0.06-1.13 (0.23±0.21)			
NP to b_{abs370,OC} (B)			0.38-5.42 (1.15±1.03)			

Table 3. Measured concentrations of nitrophenols and nitrated salicylic acids for each campaign in comparison to other studies. The concentrations are given as: minimum-maximum (mean±standard deviation).

Location	Concentration in ng m ⁻³								Reference
	4NP	2M4NP	3M4NP	2,6DM4NP	2,4DNP	3,4DNP	3NSA	5NSA	
Europe									
TROPOS (winter), Germany, Jan-Feb 2014	1.08-27.2 (7.09±7.08)	0.75-12.3 (3.64±3.05)	0.50-8.58 (2.60±2.22)	0.11-2.29 (0.65±0.58)	n.d.	n.d.	0.01-3.72 (1.36±1.02)	0.02-2.95 (0.94±0.75)	This study
Melpitz (winter), Germany, Jan-Feb 2014	0.51-10.3 (4.09±3.27)	0.29-8.90 (3.64±3.06)	0.15-6.40 (2.44±2.20)	0.04-2.74 (0.91±0.90)	0.003-0.01 (0.01±0.00)	n.d.	0.09-2.30 (0.66±0.69)	0.06-0.77 (0.32±0.24)	This study
Detling, UK, Jan-Feb 2012	(0.02) ^b	(5.0) ^b	-	-	(3.0) ^b	-	(3.0) ^b	-	Mohr et al. (2013)
Ljubljana, Slovenia, Dec 2010 to Jan 2011	0.5-3.7 (1.8)	0.31-1.5 (0.75)	0.25-1.2 (0.61)	-	0.02-0.05 (0.02)	-	0.1-3.9 (1.3)	0.2-3.4 (1.4)	Kitanovski et al. (2012)
Mainz, Germany, Winter2006/2007	(5.5) ^a	-	-	-	-	-	-	-	Zhang et al. (2010)
Rome, Italy, Feb to Apr 2003	(17.8)	-	(7.8)	(5.9)	-	-	-	-	Cecinato et al. (2005)
Hamme, Belgium, winter 2010/2011	0.92-3.0 (1.19) ^b	-	-	-	-	-	-	-	Kahnt et al. (2013)
Melpitz (summer), Germany, Jul 2014	0.01-0.12 (0.06±0.03)	0.03-0.04 (0.04±0.00)	0.02-0.03 (0.03±0.00)	n.d.	n.d.	n.d.	0.07-0.42 (0.17±0.15)	0.02-0.24 (0.09±0.09)	This study
Waldstein (summer), Germany, Jul 2014	-	-	-	-	-	-	0.01-0.35 (0.17±0.11)	0.06-0.51 (0.23±0.12)	This study
Ljubljana, Slovenia, Aug 2010	0.12-0.17 (0.15)	<0.03-0.05 (0.05)	<0.03	-	<0.01	-	0.06-0.12 (0.09)	0.14-0.24 (0.09)	Kitanovski et al. (2012)
Mainz, Germany, summer 2006	(2.8) ^a	-	-	-	-	-	-	-	Zhang et al. (2010)
Hamme, Belgium, summer 2010/2011	0.17-0.62 (0.29) ^b	-	-	-	-	-	-	-	Kahnt et al. (2013)
China									
Xianghe (summer), China, Jul-Aug 2013	0.13-4.49 (0.98±0.78)	0.01-0.85 (0.32±0.21)	0.004-0.46 (0.09±0.07)	0.01-0.23 (0.06±0.05)	2.00-10 ⁻⁴ -0.10 (0.02±0.03)	0.004-0.17 (0.03±0.04)	0.13-8.99 (1.21±1.45)	0.11-2.70 (0.88±0.64)	This study
Wangdu (summer), China, Jun2014	0.55-15.0 (2.63±2.66)	0.01-4.35 (0.68±0.78)	0.01-2.03 (0.21±0.35)	3.54-10 ⁻⁴ -0.47 (0.06±0.09)	0.002-0.41 (0.08±0.10)	0.003-0.02 (0.01±0.01)	0.37-11.3 (3.14±3.05)	0.43-3.27 (1.63±0.78)	This study
Hong Kong, summer 2010-2012 ^c	(0.3)	(0.2)	(0.02)	(0.009)	-	-	-	-	Chow et al. (2015)

^a estimated from graph^b sum of corresponding m/z ratios, including all isomers^c Concentrations are given as the average of three years

n.d.: not detected

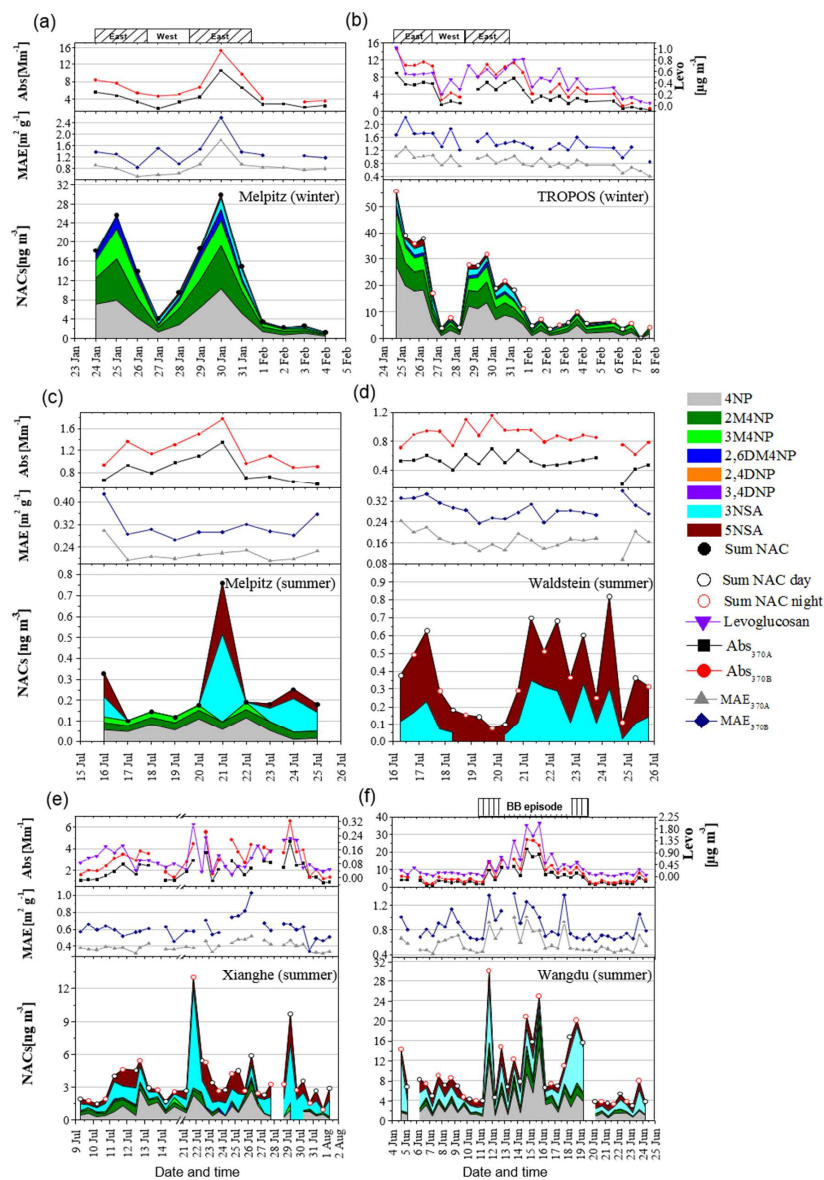


Figure 1. Temporal variation of the concentrations of nitrated aromatic compounds and levoglucosan (Levo) at each measurement site (a-f) and their optical properties. The aqueous light absorption coefficient (Abs) and mass absorption efficiency (MAE) are given at 370 nm for acidic conditions (indicated by the subscript “A”) and for alkaline conditions (indicated by the subscript “B”).

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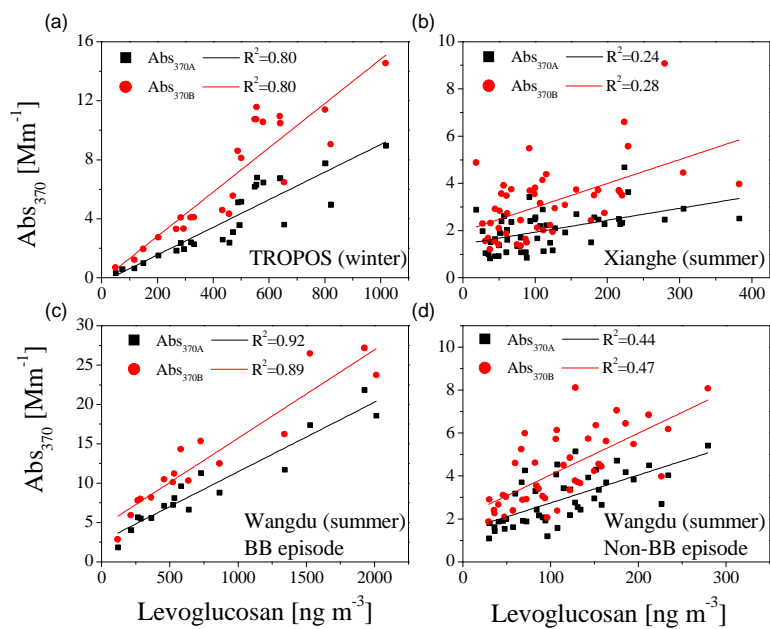


Figure 2. Scatter plot of the aqueous light absorption coefficient Abs_{370} with levoglucosan concentration for the campaigns (a) TROPOS (winter), (b) Xianghe (summer), (c) Wangdu (summer, BB episode) and (d) Wangdu (summer, non-BB episode). Abs_{370} is given for acidic conditions (indicated by the subscript “A”, black squares) and for alkaline conditions (indicated by the subscript “B”, red dots). Note different axis scales.

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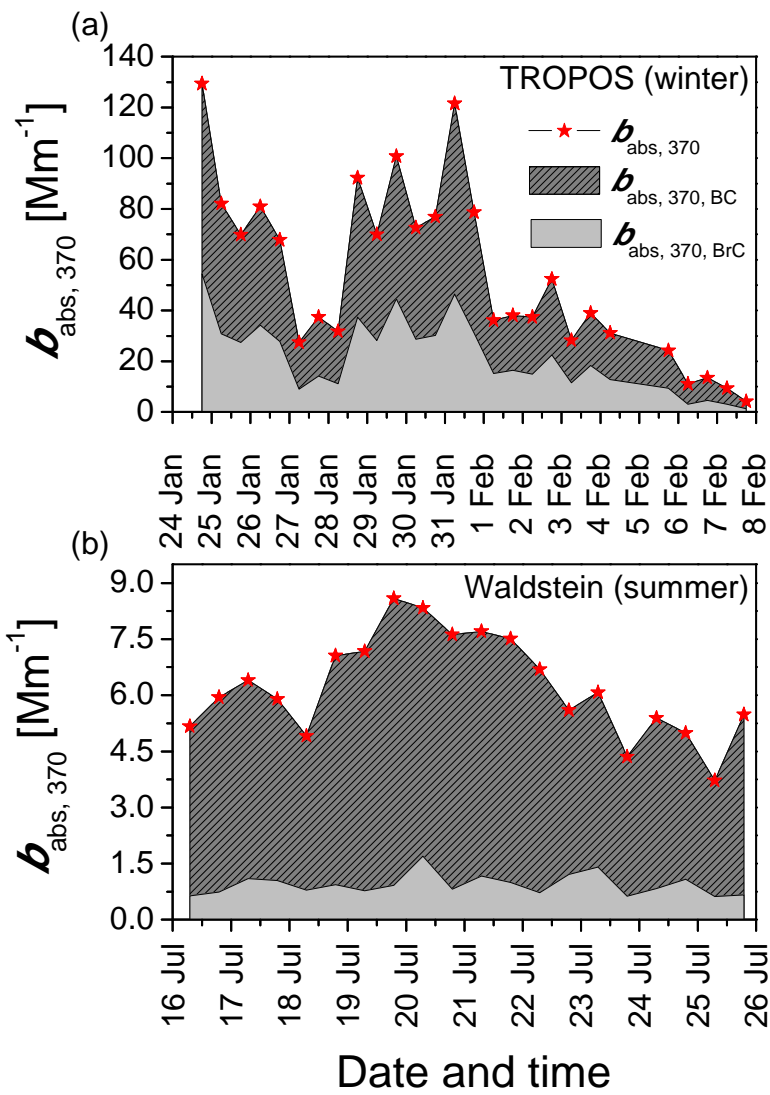
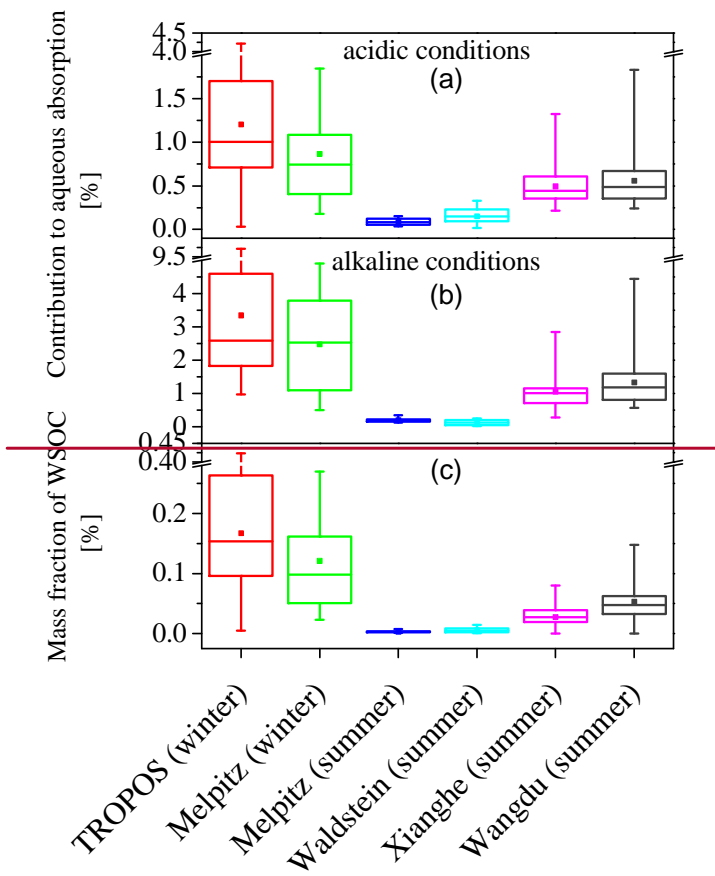


Figure 3. Temporal evolution of the particulate light absorption coefficient b_{abs} at 370 nm derived from the Aethalometer measurements during (a) the TROPOS (winter) campaign and (b) the Waldstein (summer) campaign. The fractions of black carbon (dark grey area) and brown carbon (light grey area) to the total measured b_{abs} were calculated as described in Eq. 2.



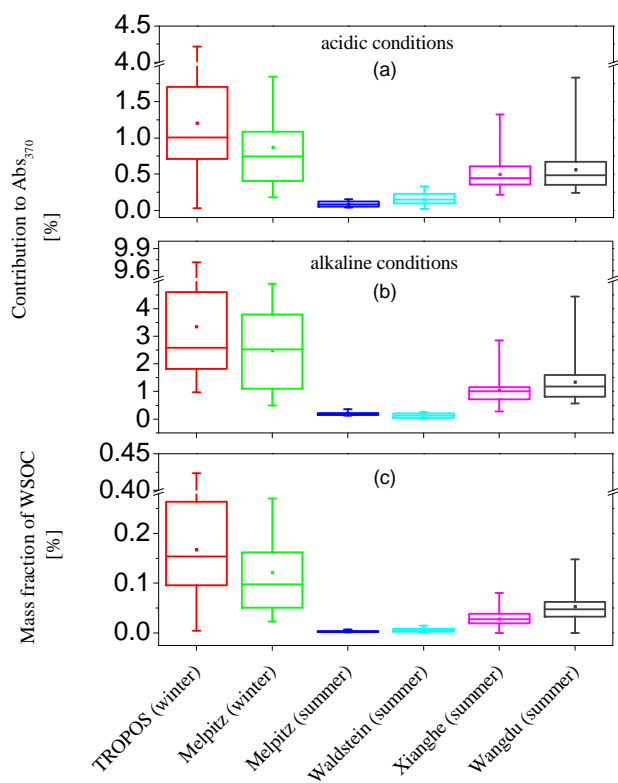


Figure 4. Top and center: Contribution of the sum of NACs to the aqueous extract light absorption at each site under acidic (a) and alkaline (b) conditions. Bottom: Mass contributions of the sum of NACs to the WSOC (c).

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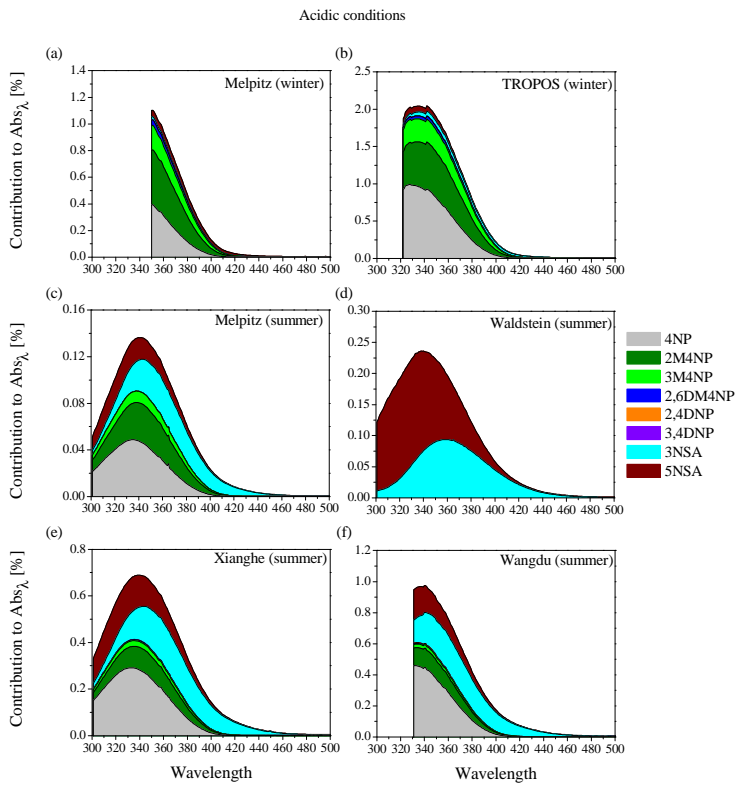


Figure 5. Relative contribution of NACs to Abs_{λ} over the spectral range of 300 to 500 nm for each measurement campaign (a-f) under acidic conditions. The data is presented as campaign averages. Due to instrumental issues, data for lower wavelengths is not always available.

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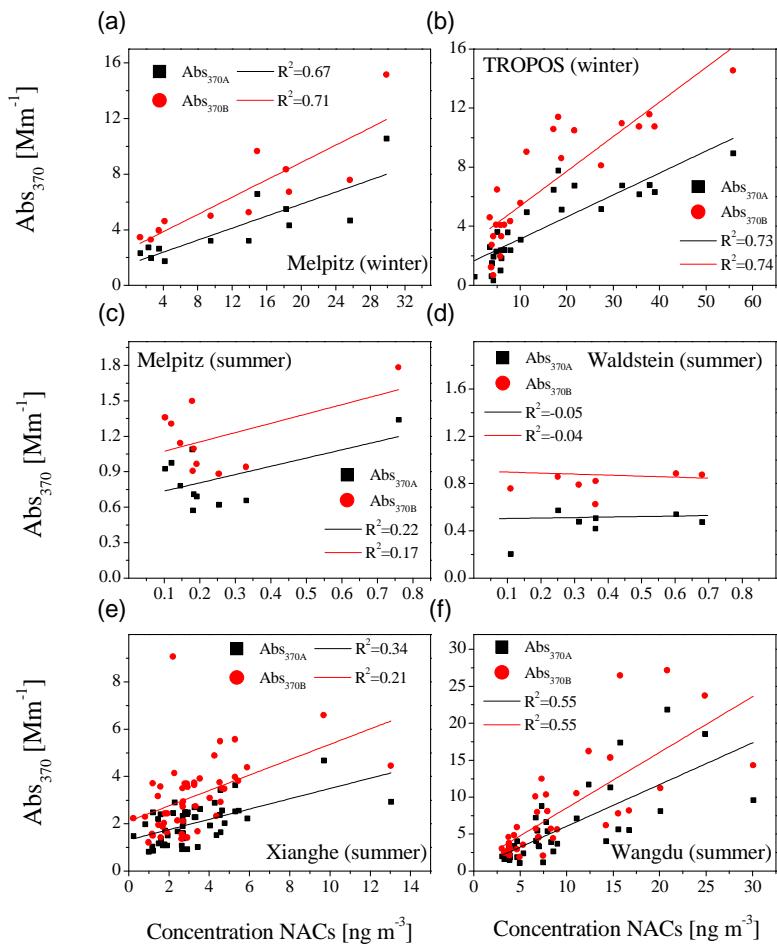


Figure 65. Scatter plots of the sum of NACs concentrations with the aqueous light absorption coefficient Abs_{370} for each campaign: (a) Melpitz (winter), (b) TROPOS (winter), (c) Melpitz (summer), (d) Waldstein (summer), (e) Xianghe (summer), (f) Wangdu (summer). The aqueous light absorption coefficient is given at 370 nm for acidic conditions (indicated by the subscript "A", black squares) and for alkaline conditions (indicated by the subscript "B", red dots).

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