Reviewer 1

This manuscript presents mass spectrometric analyses of carbonaceous aerosol in long-range transported smoke from Siberian wildfires. The analysis is based on off-line analysis of filter samples collected at two sites in Northwest Siberia: Nadym city and Bely island, which lies 800 km further north. In August 2021, both sites were impacted by smoke transported from wildfires covering large areas in Yakutia, approx. 2000 km east.

Chemical analysis of the organic aerosol is comprehensive, with three different mass spectrometric methods applied to the samples. Furthermore, multiwavelength light absorption is included in the analysis. On the other hand, there are no supporting measurements such as trace gases (e.g. CO NOx) to augment the analysis. Also, the Hysplit back-trajectories accumulate rather large uncertainty for such long distance as covered here.

Overall, this manuscript offers a relatively rare picture of carbonaceous aerosol from Siberian wildfire emissions and I recommend it for publication after some minor comments have been addressed.

Response: We thank the reviewer for undertaking this review and support for publication. In following, we try to address the reviewer's comments.

Minor comments

I do not think it is correct to refer to the smoke from the remote fires as one plume. Especially, interpreting the differences between the two sites through dilution / plume edge effects only seems oversimplification. Given that the sites are 800 km apart and wildfires were occurring over an area of several hundred km across it is quite possible that there were differences in the emissions as well as in the processing during the transport.

Response: We basically agree with the reviewer's view on plume's spatial occurrence and that the concept of plume edges and center is a simplification. It does not necessarily relate to a single plume, rather than it describes the spatial smoke density with a "plume center (or centers) at substantially elevated aerosol concentration and edges approaching more typical ambient aerosol levels without clear definition. The benefit of this classification is that it accounts for the evaporation-oxidation mechanism for secondary aerosol formation, (Palm et al., 2020) which is increased in relevance with increasing aerosol concentration. Nevertheless, we would like to point out that in fact the OMPS Aerosol Index shown in Fig. S2 demonstrates a rather large cohesive area of constantly high aerosol concentration instead of multiple segregated individual plumes at the given spatial resolution of 50km x 50km.

Referring to Fig. 2 of the manuscript, air masses moving both to Nadym and Bely crossed the fire site from East to West, thus they likely took up similar emissions. Additionally, the forest area of Central Yakutia has similar vegetation, largely dominated by larch and pine trees.. (Kharuk et al., 2021) Hence, we can assume that despite widespread wildfires, there was an uptake of rather similar BB aerosol over the intersection of the relevant air masses and the BB area, justifying the consideration of the emission as single large plume.

Based on Fig. 1, there is extensive gas and oil field flaring between Nadym and the wildfire area, but less so for Bely island. Here, more detailed air mass history analysis with higher resolution meteorological data (e.g. Flexpart with ERA5) would have helped to show if smoke observed at both sites had similar exposure to gas flaring emissions. Also, NOx from a trace gas analyser, had it been available, would have been useful. For instance, Table 1 shows that Nadym had higher CHNO fraction than Bely island. Is this due to higher NOx from the flaring, or due to different chemistry in a more concentrated plume?

Response: We can expect that gas flaring contribute to PM in both Nadym and Bely, but quantitatively depending on the meteorological conditions. Based on the BWT analysis in Fig. 2, also the air masses traveling to Bely reach first the gas fields of YNAO before moving North to Bely.

Unfortunately, the sampling was initiated because of public news about larger fires in Yakutia and arriving smoke in Nadym, and not as part of a measurement station for air quality monitoring, so only PM samples are available, but no gases could be measured.

We cannot ultimately confirm or rule out if different gas flaring contributions of NOx or the impact of different concentrations inside the plumes of Bely and Nadym are responsible for the different CHNO relative contributions. However, relative difference in CHNO between Nadym and Bely were less than 4 percentage points for APPI and ESI+, and about 8 percentage points for ESI-. APPI and ESI with direct infusion and FT-ICR MS is not an analytical approach for quantitative analysis and based by matrix effects. The reason for the number of 4 significant digits given is the fact that the measurements have the precision when repeated. Furthermore, the comparison in Table 1 does not cover exactly the same time periods, so results of minor difference cannot be discussed.

Specific comments

P1, L37-38 “Owing to lower aerosol concentration in the plume periphery than in its center, it is demonstrated how dilution affects the chemical plume composition during atmospheric aging.” The sites are 800 km apart. As commented above, changes in the emission or effect of additional NOx from gas flaring have not been ruled out.

Response: We thank the reviewer for pointing this out. The BWT analysis shows that the air mass to Bely Island and Nadym city proceeded in parallel with few degrees difference in latitude until the main gas flaring area was reached. Afterward, parallel BWTs divided and went northern to Bely Island and western to Nadym city. Therefore, we are convinced that both air masses received similar mixing with gas flaring aerosol.

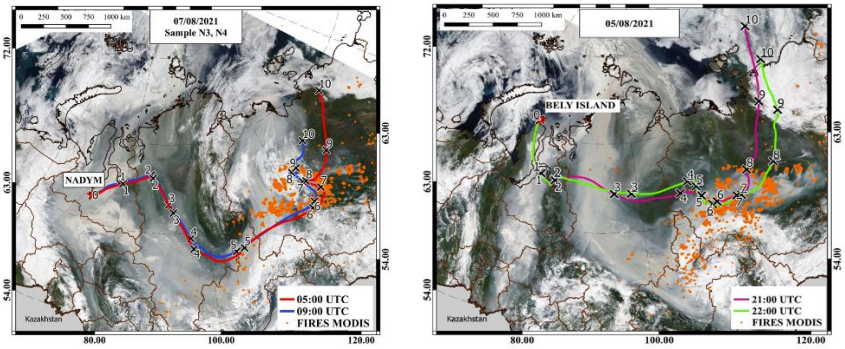
P3, L20-21 “the phenomenon of dry thunderstorms, which have been estimated to account for more than a half of the fire causes.” Please provide reference.

Response: A reference (Narita et al (2021)) for this statement is given in the sentence following.

P3, L30-31 “differences in atmospheric aging of plume center and plume periphery.” Please see previous comments on other possible causes for the differences between the sites.

Response: We agree that the atmospheric fate of the plume is a sum of different conditions, including interference with other sources. However, the concentration of particulate matter is one to two

orders of magnitude higher than in reference samples (i.e., when the plume had passed). Additionally, processing of the plume did not only take place in the gas production area, but already in a distance of >2000km in a remote area. Along the trajectories of the wildfire plume to Nadym and Bely, between approximately 60 and 67° latitude, there is no larger city in the Republic Sacha and Krasnoyarsk Krai, or known larger emission sources from industrial production. Gas flaring aerosol may be contributed not before crossing the border from Krasnoyarsk Krai to YNAO. Therefore, we conclude that the majority of the atmospheric residence of the plume happened under conditions with low or even no influence of gas flaring. After entrance to YNAO, both plumes (to Bely and Nadym) were first mixed with gas flaring emissions, but were subsequently processed for approximately 1.5 days (see exemplary figure for samples N03/N4 and B01 below) before arriving at the respective sampling sites.



P4, L36 Please explain in more detail what the different OC and EC components (Table S1) from IPMROVE_A protocol represent and what are the assumptions and uncertainties related to determination of e.g. OCpyro.

Response: We omitted further details on the carbon analysis because it is a well-established method in air quality monitoring programs and emission. (Chow et al., 2007) Despite the multiwavelength carbon analyzer is a rather new instrument, the uncertainties of the carbon fractions remain unaffected compared to the single-wavelength instrument. (Chow et al., 2015) Generally, uncertainties are sample-dependent, typical values are 2-6% for OC and TC, and 5-10% for EC; largest uncertainties are usually found in the volatile fraction OC1 and OC_{pyro} of about 50. (Zhang et al., 2021) Regarding uncertainties to the optical measurement, we refer to Chow (Chow et al., 2021) and provide an overall uncertainty of the presented Angström Absorption Exponent (AAE), calculated from the precision of the laser transmittance measurement described in. (Chen et al., 2015)

Generally, the numbering of the OC and EC fractions refers to increasing thermal refractiveness of the carbon, for OC corresponding to the reciprocal volatility. As a rough classification, in OC1 and OC2, particle-bound species are mainly thermally desorbed, while in OC3 and OC4, thermal decomposition prevails the volatilization.

We added information to the uncertainty of carbon quantities p. 4 l. 37:

"... for the separation of pyrolytic OC from EC. Precisions of the carbon analysis is sample-dependent and range between 2 and 6% for TC and 5 to 10% of the split between OC and EC according to the manufacturer. In addition to 635 nm,..."

P6, L4 “HYSPYT” do you mean HYSPLIT?

Response: Yes, the spelling is corrected to “HYSPLIT”.

P6, L22-24 “The OMPS Aerosol Index (Fig. S2) suggests that the periphery (lower OMPS Aerosol Index, yellow) of the Yakutian wildfire plume was transported to Bely Island in contrast to the plume center aerosol transported to Nadym (higher OMPS Aerosol Index, red).” Please give numerical values for the aerosol index. Please also change Fig. S2 so that the colorbar is legible.

Response: We agree with the reviewer and have added the numerical values of the OMPS (e.g., 21-08-07: Bely 1.85, Nadym >5) to the text as well as adapted the size of the colorbar in Fig. S2 to improve visibility.

P6, L24-27 “This may have led to a gradient in photochemical processing of the plume, i.e., a lower extent of atmospheric processing by OH radicals, with the northern section containing more atmospherically aged aerosol and the southern section more fresh wildfire emissions, which were picked up on the way westward.” Previously, the effect of decreased OH concentration has been shown for fresh plumes (age some hours) only. In this case, is the difference in actinic flux large enough to have an effect after maybe a week or more of atmospheric ageing?

Response: We thank the reviewer for this question. First, we based our statement on the fact that trajectories of the air masses to Nadym and Bely Island were largely parallel with some higher degrees in latitude for the latter one as shown in Fig. 2. OMPS data show evidence for substantially lower aerosol concentration in the air masses to Bely Island than to Nadym, so the apparent difference is a significant dilution factor between the two parts of the plume, supported by the OC concentrations in Nadym and Bely Island with a factor of 10 difference. Despite anticipated dilution over the entire transported distance, the OA arriving at Nadym still has a concentration > 100 $\mu g/m^{-3}$. In Hodshire et al. (2021) aging of several wildfire plumes is shown starting from less than 1 hour of aging with a corresponding OA concentration range from 10 to 650 $\mu g/m^{-3}$ (Hodshire et al., 2021). Therefore, it is likely that aging of the plume involved differences in edge/periphery and core/center of the plume over long distances of transportation. Furthermore, we are convinced that the effect of different OH production rates caused by transportation at different latitudes and consequently different actinic fluxes is of minor importance and not exceeding one order of magnitude difference in aerosol concentration and related OH reactivity.

We agree with the reviewer that suppression of OH appears in fresh plumes. The referenced sentence describes the uptake of wildfire aerosol in Yakutia by the modeled air mass, so indeed it refers to rather fresh and near-source BB aerosol. However, because of the large dimension of the fires, sources are considered to cover a distance of up to 500km.

BB aerosol aging proceeds rapidly and significant changes in aerosol composition and concentration are visible within in the first few hours after emissions. Our analytical techniques are consistently showing that the PM in Nadym still contains a molecular signature of BB, whereas in the PM of Bely Island BB are virtually absent. Considering the similar source and transportation of Yakutian wildfire PM, it points towards the fact that plume aging conditions may apply over longer aging times than hours, so the concepts in aging of fresh plumes are still applicable for longer physical ages.

P7, L12-15 “Regarding biomass burning, spectral absorption obtained throughout the near-ultraviolet to near-infrared spectral region and high Angstrom absorption exponents (AAE) up to 4.4 are were found for

smoke from smoldering combustion of pine debris in the wavelength regions from 370 to 670 nm." Please provide reference.

Response: The reference (Popovicheva and Kozlov, 2020) in the following sentence applies to both flaming and smoldering aerosol optical properties.

P7, L37 Elevated NOx may increase BrC formation during atmospheric ageing. Thus, if there are differences in the gas flaring or other NOx mixing into the plume, that could explain part of the difference. Thus, it is not self-evident that the difference in AAE is due to photobleaching only.

Response: The paragraph from L28 to L37 on page 7 deals with the AAE of the PM collected at Bely Island, where weekly averages of 1.0 and 1.2 were obtained, which is a typical result for this location. (Popovicheva et al., 2022) AAE of the high OC and EC concentrations in Nadym appeared from 1.5 to 2.7, which is a reasonable range for wildfire plumes despite different measurement techniques and wavelengths used. (Selimovic et al., 2020; May et al., 2023) The sample of supposed gas flaring contribution (N07) revealed an AAE of only 1.5.

We agree with the reviewer that significant NOx contributions may increase BrC concentration by formation for nitrogen-containing compounds, like nitrophenols, which are known as strong chromophores. As indicated by our BWT analysis, both air masses going to Bely Island and Nadym city passed through the gas flaring fields, thus were mixed with similar gas flaring aerosol emissions incl. NO_x. A significantly more intense mixing of BB aerosol going to Nadym city with gas flaring emissions is not evident.

AAEs measured for Bely Island are lower than the AAE of sample N07 and any other plume-affected sample from Nadym. As evident from several BB aerosol ageing studies, BrC was released as primary emissions or was formed after short ageing e.g., (Laskin et al., 2015), but to reach the AAE at Bely Island, degradation by photobleaching must have been taken place.

We noticed a higher contribution of most likely gas flaring in sample N07 based on the signature of polycyclic aromatic hydrocarbons (PAH). However, apart from larger PAH, the chemical composition of N07 with plume samples arriving at Nadym city before (N01-N05) showed a high similarity, supporting that different mixing with gas flaring emission had a negligible effect on the composition of the BB plume.

P8, L25 "time period (21-07-31 to 07-08-21)" Please check date.

Response: We have corrected the date to 21-08-07.

P9, L4-5 "The majority of compounds is found in the low to ultra-low volatility area, but there is a difference when comparing individual compounds classes." Please discuss the uncertainty in the volatility parameterisation.

Response: As the calculation of the saturation vapor pressure (log(C*)) in this study is based on the elemental composition, the uncertainty for the individual saturation vapor pressure value may be moderate, as it is based on fitting by multi-linear least squares analysis of 30,000 model compounds. (Li et al. ACP 2016) However, the parametrization and separation into volatility classes (e.g., intermediate-volatile $C^*=3x10^{-6}$ - 300 µg m^{-3}, semi-volatile $C^*=300$ - 0.3 µg m^{-3}) is based on volatility classes that span a several orders of magnitude. Therefore, the volatility parametrization can be considered as sufficiently accurate for these purposes.

P9, L35-36 “This has been assigned to HU-HOM, which are produced from the photooxidation of larger PAHs on soot particles, thus indicating heterogeneous processing of wildfire aerosol particles.” Please provide reference.

Response: The reference (Li et al, 2022) in the following sentence applies to definition ad origin of HU-HOMs.

P12, L36 – P13, L40 Please consider splitting the long paragraph into shorter ones.

Response: We agree with the Reviewer and split the paragraph.

P13, L16-21 “According to RETprim/RETtot close to zero, samples N01–N02 (06 August 2021) contain biomass burning aerosol e.g., originating from fires at smoldering condition (Fig. S6). From 07 August 2021 to the morning of 08 August 2021 (N03–N07), the fires became more intense and turned over to more flaming conditions, suggested by increased OC and EC concentrations, lower ratios OC-to-EC being typical for higher combustion efficiency, and RETprim/RETtot between 0.15 and 0.26; on these days, the main plume by means of highest aerosol concentrations arrived Nadym city.” Did you observe any difference in the mass spectra that could be explained by the apparent differences in the combustion characteristics? For instance, Sekimoto et al. (2018, 2023) found distinct VOC profiles for the high and low temperature combustion.

Response: We thank the reviewer for this question. We are aware of the concept outlined by Sekimoto et al. and developed a similar model for wood stove emissions based on a 3-factor solution. (Czech et al., 2016; Elsasser et al., 2013) However, all of these studies were based on online measurements, i.e., contained a large number of samples, whereas our dataset is typical for “large p, small n” and thus not suitable for deconvolution.

We may use quantitative ECOC data and AAE of this study in combination with parametrization to the modified combustion efficiency (MCE) by Pokhrel et al (2016) from laboratory burns for deriving combustion conditions. (Pokhrel et al., 2016) Based on the ratio of EC to OC in the plume at Nadym city (samples N01 to N05), we obtain AAEs for the wavelengths 405, 532 and 660nm from 2.1 to 2.3, which agrees well with our AAE data (from wavelengths 405 and 808nm) from 1.5 to 3.0. With an AAE of 2.2, we obtain a MCE between 0.9 and 0.96, indicating rather flaming burning conditions, which agrees with the average MCE for boreal forest fires from Akagi et al. (Akagi et al., 2011)

Overall, the parametrization from Pokhrel et al. generates plausible from our measurements for MCE, but further details about combustion conditions would be too speculative considering the available information. (Pokhrel et al., 2016)

P15, L29-30 “Also, AAE values are decreased, indicating degradation of chromophores by photobleaching (Liu et al., 2021).” Or then secondary BrC was not formed, due to e.g. lower NOx.

Response: We do not state that secondary BrC was formed or not formed. Generally, it is well-known that primary biomass burning aerosol contains BrC species, especially from relatively poor combustion conditions, associated with increased AAE. (Laskin et al., 2015) Regardless if secondary BrC have been formed during atmospheric transport, BrC from the primary BB emissions must have been – likely photochemically considering the meteorology - degraded to reach AAEs close to unity. For longer photochemical ages, photobleaching is a well-known phenomenon that would explain our observations. For PM collected at Nadym city, relatively high AAEs were obtained. Although these AAEs might be caused

by secondary BrC formation, it fits to the parametrization by Pokhrel et al. (2016) for primary BB aerosol and our result of a distinct BB molecular signature. Therefore, we assume that the high AAEs are mainly caused by primary BrC species from the forest fire.

P18, L8-11 “Moreover, AAE405/808 from 1.5 to 3.3 suggested the presence of BrC in Nadym city, but the weekly average of AAE405/808 over a similar period at Bely Island accounted for 1-1.2, indicating more intense atmospheric aging and degradation of BrC chromophores from the same wildfire plume.” Please see previous comment.

Response: We would like to point out again that at the source of the BB aerosol, we may assume AAE significantly larger than unity as typical for BB emissions. Photobleaching after long-range transport adequately explains the low AAE measured in the PM of Bely Island while differences in aging between the two sites can be explained by different aerosol concentrations, i.e., different OH reactivities.

References

Akagi, S. K.; Yokelson, R. J.; Wiedinmyer, C.; Alvarado, M. J.; Reid, J. S.; Karl, T.; Crounse, J. D.; Wennberg, P. O. Emission factors for open and domestic biomass burning for use in atmospheric models. Atmos. Chem. Phys. 2011, 11 (9), 4039–4072. DOI: 10.5194/acp-11-4039-2011.

Chen, L.-W. A.; Chow, J. C.; Wang, X. L.; Robles, J. A.; Sumlin, B. J.; Lowenthal, D. H.; Zimmermann, R.; Watson, J. G. Multi-wavelength optical measurement to enhance thermal/optical analysis for carbonaceous aerosol. Atmos. Meas. Techn. 2015, 8 (1), 451–461. DOI: 10.5194/amt-8-451-2015.

Chow, J. C.; Wang, X.; Sumlin, B. J.; Gronstal, S. B.; Chen, L.-W. A.; Trimble, D. L.; Kohl, S.; Mayorga, S. R.; Riggio, G.; Hurbain, P. R.; Johnson, M.; Zimmermann, R.; Watson, J. G. Optical Calibration and Equivalence of a Multiwavelength Thermal/Optical Carbon Analyzer. Aerosol Air Qual. Res. 2015, 15 (4), 1145–1159. DOI: 10.4209/aaqr.2015.02.0106.

Chow, J. C.; Watson, J. G.; Chen, L.-W. A.; Chang, M. O.; Robinson, N. F.; Trimble, D.; Kohl, S. The IMPROVE_A Temperature Protocol for Thermal/Optical Carbon Analysis: Maintaining Consistency with a Long-Term Database. J. Air Waste Manag. Assoc. 2007, 57 (9), 1014–1023. DOI: 10.3155/1047-3289.57.9.1014.

Czech, H.; Sippula, O.; Kortelainen, M.; Tissari, J.; Radischat, C.; Passig, J.; Streibel, T.; Jokiniemi, J.; Zimmermann, R. On-line analysis of organic emissions from residential wood combustion with single-photon ionisation time-of-flight mass spectrometry (SPI-TOFMS). Fuel 2016, 177, 334–342. DOI: 10.1016/j.fuel.2016.03.036.

Elsasser, M.; Busch, C.; Orasche, J.; Schön, C.; Hartmann, H.; Schnelle-Kreis, J.; Zimmermann, R. Dynamic Changes of the Aerosol Composition and Concentration during Different Burning Phases of Wood Combustion. Energy Fuels 2013, 27 (8), 4959–4968. DOI: 10.1021/ef400684f.

Hodshire, A. L.; Rammarine, E.; Akherati, A.; Alvarado, M. J.; Farmer, D. K.; Jathar, S. H.; Kreidenweis, S. M.; Lonsdale, C. R.; Onasch, T. B.; Springston, S. R.; Wang, J.; Wang, Y.; Kleinman, L. I.; Sedlacek III, A. J.; Pierce, J. R. Dilution impacts on smoke aging: evidence in Biomass Burning Observation Project (BBOP) data. Atmos. Chem. Phys. 2021, 21, 6839–6855. DOI: 10.5194/acp-21-6839-2021.

Kharuk, V. I.; Ponomarev, E. I.; Ivanova, G. A.; Dvinskaya, M. L.; Coogan, S. C. P.; Flannigan, M. D. Wildfires in the Siberian taiga. Ambio 2021, 50 (11), 1953–1974. DOI: 10.1007/s13280-020-01490-x.

Laskin, A.; Laskin, J.; Nizkorodov, S. A. Chemistry of atmospheric brown carbon. Chem. Rev. 2015, 115 (10), 4335–4382. DOI: 10.1021/cr5006167.

May, N. W.; Bernays, N.; Farley, R.; Zhang, Q.; Jaffe, D. A. Intensive aerosol properties of boreal and regional biomass burning aerosol at Mt. Bachelor Observatory: larger and black carbon (BC)-dominant particles transported from Siberian wildfires. Atmos. Chem. Phys. 2023, 23 (4), 2747–2764. DOI: 10.5194/acp-23-2747-2023.

Narita, D.; Gavrilyeva, T.; Isaev, A. Impacts and management of forest fires in the Republic of Sakha, Russia: A local perspective for a global problem. Polar Sci. 2021, 27, 100573. DOI: 10.1016/j.polar.2020.100573.

Palm, B. B.; Peng, Q.; Fredrickson, C. D.; Lee, B. H.; Garofalo, L. A.; Pothier, M. A.; Kreidenweis, S. M.; Farmer, D. K.; Pokhrel, R. P.; Shen, Y.; Murphy, S. M.; Permar, W.; Hu, L.; Campos, T. L.; Hall, S. R.; Ullmann, K.; Zhang, X.; Flocke, F.; Fischer, E. V.; Thornton, J. A. Quantification of organic aerosol and brown carbon evolution in fresh wildfire plumes. Proc. Natl. Acad. Sci. U.S.A. 2020, 117 (47), 29469–29477. DOI: 10.1073/pnas.2012218117.

Pokhrel, R. P.; Wagner, N. L.; Langridge, J. M.; Lack, D. A.; Jayarathne, T.; Stone, E. A.; Stockwell, C. E.; Yokelson, R. J.; Murphy, S. M. Parameterization of single-scattering albedo (SSA) and absorption Ångström exponent (AAE) with EC / OC for aerosol emissions from biomass burning. Atmos. Chem. Phys. 2016, 16 (15), 9549–9561. DOI: 10.5194/acp-16-9549-2016.

Popovicheva, O.; Kozlov, V. Impact of combustion phase on scattering and spectral absorption of Siberian biomass burning: studies in Large Aerosol Chamber. In Proceedings of SPIE - 26th International Symposium on Atmospheric and Ocean Optics: Atmospheric Physics; Matvienko, G. G., Romanovskii, O. A., Eds. 11560, 2020; p 252. DOI: 10.1117/12.2575583.

Selimovic, V.; Yokelson, R. J.; McMeeking, G. R.; Coefield, S. Aerosol Mass and Optical Properties, Smoke Influence on O 3 , and High NO 3 Production Rates in a Western U.S. City Impacted by Wildfires. J. Geophys. Res. Atmos. 2020, 125 (16). DOI: 10.1029/2020JD032791.

Zhang, X.; Trzepla, K.; White, W.; Raffuse, S.; Hyslop, N. P. Intercomparison of thermal–optical carbon measurements by Sunset and Desert Research Institute (DRI) analyzers using the IMPROVE_A protocol. Atmos. Meas. Tech. 2021, 14 (5), 3217–3231. DOI: 10.5194/amt-14-3217-2021.