

Atmos. Chem. Phys. Discuss., referee comment RC1
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Comment on acp-2021-193

Anonymous Referee #1

Referee comment on "Polycyclic aromatic hydrocarbons (PAHs) and their nitrated and oxygenated derivatives in the Arctic boundary layer: seasonal trends and local anthropogenic influence" by Tatiana Drotikova et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-193-RC1>, 2021

In this study polycyclic aromatic compounds (PACs), including PAHs, as well as nitro- and oxy-PAHs were determined in air in Longyearbyen Svalbard for 8 months. There are many novel aspects to the study. There is a nice demonstration of the effect of polar sunrise in February, where oxy-PAHs begin to be detected. The study also shows that, contrary to reports for remote sites like Zeppelin station at Ny-Ålesund, and Alert in Northern Canada, PAHs are higher in summer due to shipping emissions from high vessel traffic. Local vehicle traffic eg snowmobiles are identified as important sources in the spring (P3) period. Previous studies on PAHs in the Arctic have focused on long range transport and tended to ignore local sources. The interpretation of results also considers back trajectories, wind directions, humidity and the boundary layer height at the sampling site during winter and spring conditions. A large suite of PACs were determined (29 oxy-PAH and 35 nitro-PAHs) making it the most detailed study of these transformation products in the Arctic to date. However, the analysis of unsubstituted and alkylated PAHs was much more limited with the latter group consisting of only 3 methyl-PAHs + retene. Thus source attribution of the PAHs was a bit limited. The use of HPLC-fluorescence, while giving good detection limits, meant that some alkylated PACs would be co-eluting with the target analytes due to more limited peak resolution, resulting in less precise measurements compared with GC-MS (Wise et al. J Chromatog 1993). The authors should acknowledge other possible sources for the oxy-PAHs. Several of the oxy-PAHs are actually industrial chemicals or used in consumer products (eg benzophenone). It is actually quite interesting that benzophenone is detected; possibly it reflects emissions from the sampling site (UNIS) or nearby facilities.

Specific comments

line 16. Concentration levels can be replaced with "concentrations"

line 64. The discussion here mainly applies to the European arctic. The situation obviously differs across the Arctic eg Canadian arctic archipelago and western Greenland are known to receive LRAT from mid-continental North America as is well documented from air mass

trajectories and events such as forest fires (Yu et al ES&T 2019; Keegan et al PNAS 2014)

line 115. How is waste handled locally? Landfill only? Could be an important point re sources if incinerated.

line 197. The authors should provide a rationale for their use of HPLC-fluorescence. there are hundreds of PAHs which are difficult to separate even with two-dimensional gas chromatography.

line 218. The QA data should be provided in the SI eg actual agreement with SRM 1649b. This is particularly important because the data from Zeppelin station were analysed using GC-MS not LC-fluorescence. Would be useful for other researchers if all analytes were reported even those not certified

line 258. Are results comparable given the different methods of analysis. Is this for the sum of the same analytes. Similarly the comparison with Pallas depends on same analytes and method performance although the samples from Pallas were analysed by LC-fluorescence

line 356. Yu et al (2019) summarized the cold and warm season concentrations and differences vary greatly among individual PAHs. In their summary, fluorene had the greatest difference (8-fold higher in cold season). The median difference for average concentrations of 19 PAHs was 3.4. Thus the statements here re order of magnitude need more precision.

line 417, Spelling methylnaphthalene

line 438. Unfortunately this study did not look at alkylated PAHs in depth and thus conclusions about fuel and engine emission sources are very uncertain.

Table S1. What about retene? It is not discussed in the main text but was determined in all samples. As a component of coal dust and biomass burning, but not from combustion of fossil fuels – it could be helpful to identify sources

line 454. Benzophenone is an industrial compound eg used as a UV blocker in plastics. It is not really a PAH oxidation product unless its precursor diphenylmethane is included. Looks like the sampling is picking up a lot of emissions from products rather than from combustion. Similarly phthalic anhydride is probably from plastics rather than atmospheric oxidation of benzofuran