Review of "Atmosphere-ocean Exchange of heavy metals and polycyclic aromatic hydrocarbon in the Russian Arctic Ocean".

This work reports the concentrations of PAHs and metals in air, water and snow in the Russian sector of the Arctic. There is no previous data for this sector, so this contribution is very important. The work is of mix quality, with sections that are generally well done, but other material that is erroneous or needs further work. The manuscript needs some work in order to present the data appropriately, improve the comparison with other studies for polar regions, and give some extra depth to the discussion. This revision is mainly for the PAHs part. I suggest moderate to major modifications before it can be accepted.
Response: we are very grateful that you spend your valuable time helping us to revise this manuscript with good comments and suggestions.

1. Line 40. Comment and cite a work on long-range atmospheric transport of PAHs (or pops) to the arctic.
Response: We will add the references concerning long-range atmospheric transport of PAHs (or POPs) to the arctic.

2. Line 49-50. Provide examples, there are some published for Antarctica and the Arctic for both metals and pahs.
Response: We will add the published paper for metals and PAHs in polar regions as examples.

3. Note that not all PAHs are persistent, it also depends if they are found in the gas or dissolved phase (less persistent) or associated to aerosols and particulate matter.
Response: thank you for pointing out this important note. In revised manuscript, we will add the examples which clarified that aerosols contained PAHs deposited into sea ice and soils (or snow) which is an important source for the contribution of persistent PAHs. Indeed, according to the previous study (**Fernandes and Sicre, 1999**), the major PAHs either from adjacent areas or low latitudes are in the form of aerosols and binding with black carbon (particulate matter).

Fernandes, M. B., and Sicre, M. A.: Polycyclic Aromatic Hydrocarbons in the Arctic: Ob and Yenisei Estuaries and Kara Sea Shelf, Estuarine, Coastal and Shelf Science, 48, 725-737, https://doi.org/10.1006/ecss.1999.0472, 1999.

4. Line 73. Biogeochemical instead of biochemical
Response: we will revise it.

5. Line 77-79. Specify if you are referring to rain or snow, or both. I guess snow.
Response: we will specify the wet deposition as snow deposition in **re**vised manuscript.

6. Line 110. This citation is not adequate here.
Response: we realized the methods here concerning simultaneous sampling both for gas and aerosol phase PAHs. The citations of details about these two methods we will add.

7. Line 116. I guess that first in aluminum foil and after in polyethylene bags, which must be air-tight.

Response: after air sampling in the ship, we did keep the samples in folded aluminium foil firstly. We will revise this sentence as "the filters and PUFs were firstly covered with aluminum foil tightly for air-tightness, then immediately placed in polyethylene bags and zip the bags, and frozen at -20 °C prior to chemical analyses."

8. Line 119. Was snow melted immediately? How was snow melted?

Response: no, snowfall samples were not melted immediately. After sampling, all samples were protected from light and stored at 4 °C in borosilicate glass bottles prior to the analysis. Snowfall samples were melted thoroughly at room temperature. We will add this information

9. Line 123. M3 or L, these are huge volumes. I have never seen such large volumes for water using a XAD. Unless there is a typo mistake, such volumes need a justification and discussion.

Response: Thank you for pointing out this mistake. The unit should be "mL". This mistake will be corrected. We only used XAD-2 resin rather than XAD-4 resin for high volume of water. Water was filtered at a flow rate averaging 4 L/min with a pneumatic pump (Flojet) through a borosilicate microfiber glass filters (1 mm nominal pore size), housed in an aluminum filter support.

10. Line 265. It cannot be equation 13.

Response: we are sorry for this mistake. The hydroxyl radicals concentrations [OH] in the considered mixed layer (between 1,000 and 500 hPa) was based on the zonally and monthly averaged concentrations of OH radicals from **Spivakovsky and coworkers (2000)**. Therefore, this sentence has been removed.

Spivakovsky, C. M. et al. Three-dimensional climatological distribution of tropospheric OH: update and evaluation. J. Geophys. Res. 105, 8931-8980 (2000).

11. Line 266. Is this concentration appropriate for the arctic? Discuss.

Response: This is a very good question to discuss! We must admit that there is no ranges or exact data of OH radical levels in troposphere of polar regions.

Firstly, the primary source of HO radical in the troposphere is the photolysis of O_3 to produce O (^1D). This reaction requires radiation of wavelength less than 315nm, otherwise (O^3P) is produced. The latter species reacts with molecular oxygen in the presence of N_2 or O_2 to produce O_3. The electronically excited O(^1D) usually relaxes to produce (O^3P) but also undergoes reaction with water to produce HO. While minor sources of HO are available through reaction of O(^1D) with CH_4 and N_2. Therefore, the methods to measure OH concentrations were usually based on observed distributions of O_3, H_2O, NO_t (NO_2+NO+$2N_2O_5$+NO_3 +HNO_2+HNO_4), CO, hydrocarbons, temperature, and cloud optical depth.

Thus, it is difficult to compare the OH concentrations by different methods and altitudes as well as latitudes. **Hewitt and Harrison (1985)** summarized the OH concentrations in different

altitude as well as the global mean, which showed the range of 0.5-5 × 10^6 mol cm^{-3} for daytime OH radical. **Li et al. (2008)** used an empirical method is presented to determine effective OH concentrations in the troposphere and lower stratosphere, based on CH_4, CH_3Cl, and SF_6 data from aircraft measurements (IAGOS-CARIBIC) and a ground-based station (NOAA). The results showed tropospheric OH average values of 10.9 × 10^5 (σ = 9.6 × 105) mol cm^{-3} in a global level. The reason we used data from **Spivakovsky and coworkers (2000)** is that the estimation of OH concentrations considered by latitudes ($\pm 32^o$) in Northern Hemisphere.

It should be noted that precipitation amounts in the Arctic are very low (annual precipitation on Svalbard is 150-300 mm). This means that wet scavenging is not efficient and the lifetime for soluble species like aerosols is longer than on the continents to the south. Gas- phase chemical removal of trace compounds all but stops in the Arctic atmosphere during the polar night. In the absence of sunshine, the production rate of the OH radical, which is the main gas-phase scavenger, is low. Also, in the sunlit part of the year, the chemical lifetime of trace compounds is relatively long in the polar atmosphere (except in the near-surface layer that is impacted by snowpack photochemical processes), due to the strong attenuation of short wave visible sunlight as the solar elevation is low and the low specific humidity. Therefore, the OH radicals in the Arctic troposphere should be further measured throughout the year. So far, OH radicals levels are within the global levels.

C.N. Hewitt, Roy M. Harrison, Tropospheric concentrations of the hydroxyl radical—a review, Atmospheric Environment (1967), Volume 19, Issue 4, 1985, Pages 545-554.

Li, Mengze; Karu, Einar; Brenninkmeijer, Carl; Fischer, Horst; Lelieveld, Jos; Williams, Jonathan; 2018; npj Climate and Atmospheric Science, (1): 29.

Spivakovsky, C. M. et al. Three-dimensional climatological distribution of tropospheric OH: update and evaluation. J. Geophys. Res. 105, 8931-8980 (2000).

12. Line 269-270. I cannot understand this sentence if these estimations have just been explained.

Response: the uncertainty (error propagation) analysis basically used the relative standard deviation (RSD) based on measured uncertainties in air and water analysis, air−water partitioning coefficients (including Henry's law constant and temperature), and overall mass transfer velocity were considered. We will add the equation in Supplementary Materials.

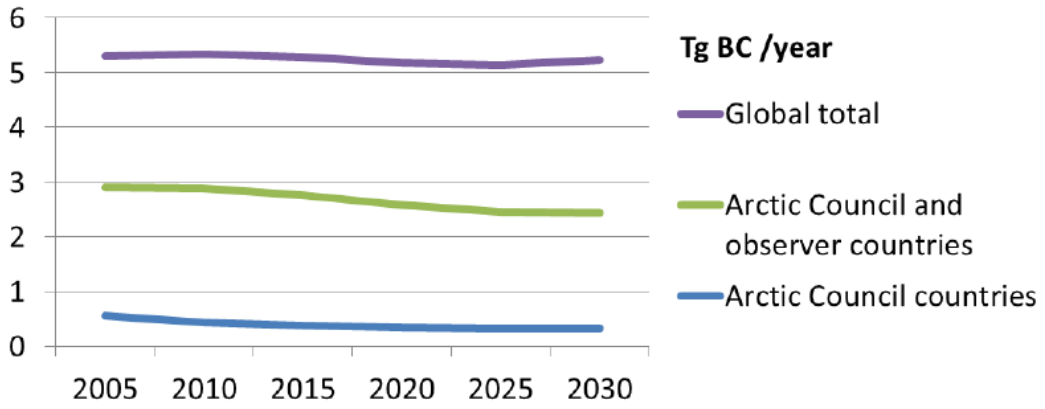
13. Line 370. In addition to the highest, provide the range for each basin. Generally, the values commented here do not correspond always to the values seen in Figure 5.

Response: the range of $\sum_{35}$ PAH concentrations in gas, aerosols and dissolve water for each basin will be added. We have checked the original data in Figure 5, some wrong concentration values will be revised in this paragraph.

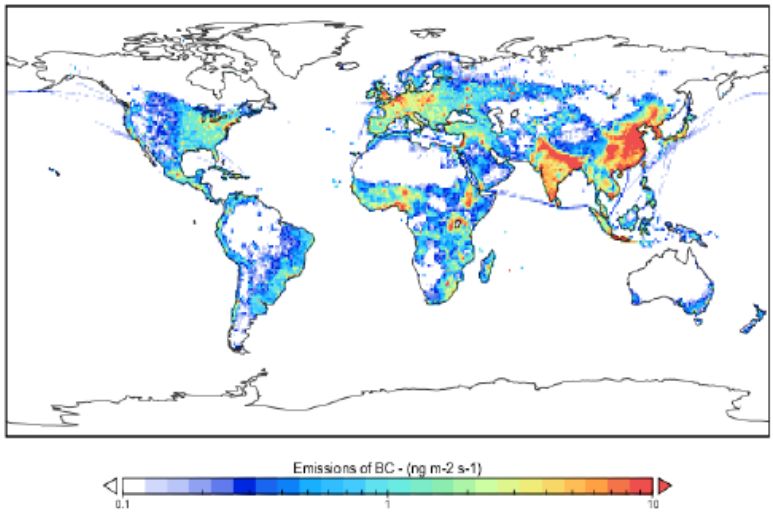
14. Line 372. The concentrations in aerosols are extremely high! These need a comparison with other studies and a discussion. Which is the black carbon concentration in aerosol for this region?

Response: we are very sorry that this concentration was showing wrong in the paper. It cannot be so high. All concentrations should be divided 100. We will make corrections for graphs and texts. There are some reports concerning PAH concentrations in atmosphere in Ocean. However, not all separating gas and particle phase. Therefore, we only compared and discussed with the separated ones as "$\sum_{35}$ PAH concentrations in aerosols (C_A, ng m^{-3}) in the Barents Sea (0.25-2.95), and East Siberian Sea (0.24-3.32) with average C_A values of 1.38 and 2.07 ng m^{-3} respectively were apparently higher than those in the Leptev Sea (0.23-0.89) and Kara Sea (0.23-0.27) with average CA values of 0.30 and 0.25 ng m^{-3}, respectively (Fig. 5b). The average CA of $\sum_{35}$ PAH in present study is higher than those of $\sum_{64}$ PAH measured in South Atlantic Ocean (mean = 0.93 ng m^{-3}) and North Pacific Ocean (mean = 0.56 ng m-3) while much lower than those of $\sum_{64}$ PAH in Indian Ocean (mean = 10 ng m-3) (Gonzalez-Gaya et al., 2016). Considering average $\sum_{35}$ PAH C_A (1.02 ng m^{-3}) in the Russian Arctic Ocean, the value is comparable to those of $\sum_{64}$ PAH observed in South Atlantic Ocean and South Pacific Ocean (both mean = 1.1 ng m^{-3}) (Gonzalez-Gaya et al., 2016). The levels of $\sum_{18}$ PAH C_A were measured from North Pacific towards the Arctic Ocean with the range from 0.0002 to 0.36 ng m^{-3}, with the highest concentration found in the coastal areas in East Asia (Ma et al., 2013). These concentrations were significantly lower than the averages levels found in our study. Besides, Ma et al. (2013) observed the relatively higher $\sum_{18}$ PAH C_A in the most northern latitudes of the Arctic Ocean, which is associated with back trajectories of air masses from Sothern Asia. The higher levels of C_A in our study could be attributed to the costal line close to larger burning taiga forest and more industrial sources in the boreal regions of Russian continent. Similar to the pattern for heavy metals mentioned above, high levels of these chemicals may have been derived from atmospheric transport from the industrial areas of the Russian continent. Because different sampling methods, different measured total PAH species and not all reports separated gas and particles concentrations, it is quite difficult to compare PAH levels in the aerosols.".

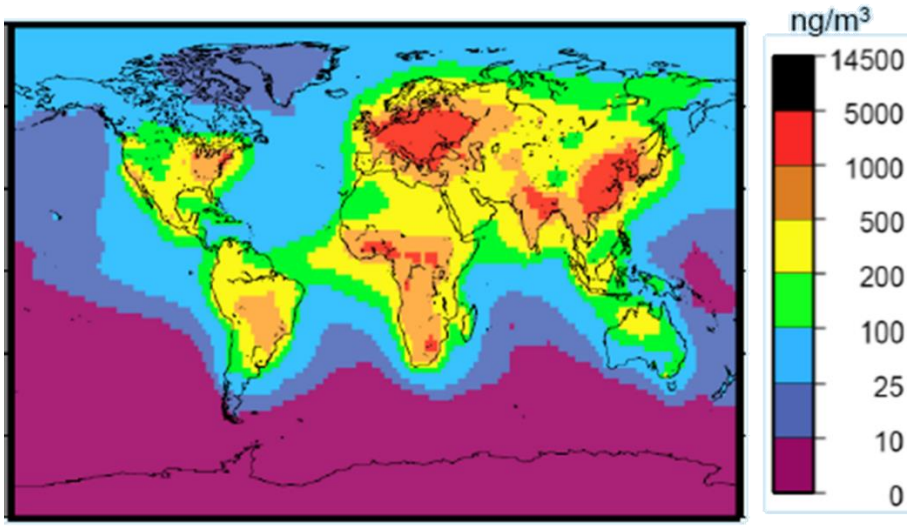
As for black carbon concentration in aerosol, we did not establish the filter-based techniques or direct techniques to measure them in our study. From other studies (**Figures**), we could see that Concentrations are low in the Arctic compared with lower latitudes and come mostly from outside the area and there are lots of black carbon emission which can be transported to the Arctic regions. We think the connections between black carbon and PAHs contents can be further studied.



Sources: MACEB project (www.maceb.fi), IIASA-GAINS model.

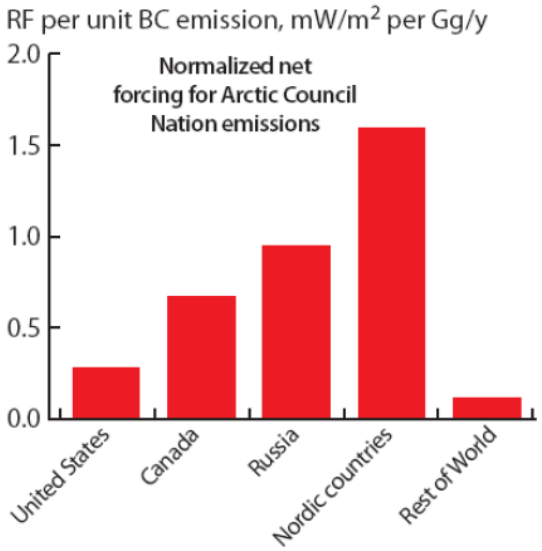


Source: UNEP/WMO 2011. United Nations Environment Programme , World Meteorological Organization (WMO), Integrated Assessment of Black Carbon and Tropospheric Ozone. 2011. http://2011_integrated-assessment-SUMMARY_UNEP-WMO.pdf



Source: Koch, D et al. Corrigendum to "Evaluation of black carbon estimations in global

aerosol models" published in Atmos. Chem. Phys., 9, 9001-9026, 2009, Atmos. Chem. Phys., 10, 79–81, https://doi.org/10.5194/acp-10-79-2010, 2010.



Source: AMAP, 2011. The Impact of Black Carbon on Arctic Climate (2011). By: P.K. Quinn, A. Stohl, A. Arneth,T. Berntsen, J. F. Burkhart, J. Christensen, M. Flanner, K. Kupiainen, H. Lihavainen, M. Shepherd, V. Shevchenko,H. Skov, and V. Vestreng. https://www.amap.no/documents/download/977/inline

15. Generally, compare the pahs and metal concentrations with other reports for the Arctic, even if these are for the north atlantic and north pacific.
Response: we will add the comparisons for both metals and PAHs with other oceans.

16. Line 391. Here or in the methods, comment the range of estimated dry deposition velocities.
Response: dry deposition velocities (v_D) is very crucial factor to calculate dry deposition as shown in equation. We will add the information to describe and compare the estimated dry deposition velocities in our study.

$F_{DD}=864 v_D C_A$

17. Line 395. Huge values, If possible compare with other measures. Report as well the concentrations in snow.
Response: we will add the content to compare with other measurements.

18. Line 398. Comment the range of diffusive fluxes, and show them in a figure, maybe in the supplementary material.
Response: we will add a graph and a discussion with specific diffusive fluxes of F_{AW} in the current range.

19. Line 399 and figure 6b. This is not clear to me. For which pahs there is a net volatilization and for which there is a net deposition.

Response: we are sorry for this confusion. Actually, it is not volatilization according to the calculated $F_{AW,}$ while we did not make the direction downwards. We will revise this graph.

20. Line 413. Rewrite. As I understand them, these fluxes for the the basins studied, but not all the Arctic, which should be clarified. Provide the surface for each basin in methods.
Response: these fluxes were based on each basin of the Russian Arctic Oceans. We will rewrite this part for better clarification for the differences between each basin and the whole Arctic oceans. The surface for each basin was based on the sampling sites during the cruise and we will add this information to the methods.

21. Review the spelling of pah's names in figure 4 and 5. The size of the legend (scale) in the figures should be bigger.
Response: we will remake Figure 4 and 5 for lager scale of the legend.

22. Review the use of English in the manuscript.
Response: after the revision of our manuscript, we will ask a native speaker to check the language thoroughly for English language in our manuscript.

23. Table S4. Why dibenzothiphene and anthracene appear twice in this table, while phenanthrene is not there? Review all the tables and data set. In addition, the mean total concentrations seem to not correspond to the distribution seen in Figure 5.
Response: thank you very much for your careful checking. Indeed, we have found that PAHs did not match the concentration data. We have checked our original dataset and have revised all tables. We also checked whether the data used in Figures are correct as shown in the tables.

24. Figure S5. The three legends appear as Cg… correct.
Response: thank you for this careful check! we will correct this graph.

25. Improve the quality of the figures in the supplementary material. Generally, the presentation aspects of this work need to be reviewed.
Response: we will make the figures in supplementary material easier to watch with better resolution. Thank you again for these helps. We hope you would continue helping us to revise our manuscript.