

The MS titled “Atmosphere–ocean exchange of heavy metals and polycyclic aromatic hydrocarbons in the Russian Arctic Ocean” written by Ji et al. researched the results of a Russian Arctic assessment of the occurrences and atmosphere–ocean fluxes of 35 polycyclic aromatic hydrocarbons (PAHs) and 9 metals (Pb, Cd, Cu, Zn, Fe, Mn, Ni, and Hg). The topic of this study is quite interesting due to the reflection of anthropogenic influences in the normal biochemical cycles as the balance of geochemical substances between ocean and gas. Authors pointed out the net input of Hg and 35 PAHs into ocean, filling the data gaps in this field. The deposition including dry and wet deposition in the Arctic Ocean so far appeared very sporadic data without a continuous sampling sites and period. The topic of this MS is within scope of ACP, the language usage and structure of article is generally good and well-written. However, there are still some minor problems and some questions remained. I would like to support this MS to be published unless my questions and problems are well addressed or answered. There are specific questions I found in this MS.

Response: thank you very much for your valuable suggestions on our manuscript. We will revise our manuscript according to your good suggestions.

1. L43-44, it's quite not logic here, authors should introduce the transported pollutants from low attitude to the polar region as the Arctic rather than the present statements about reducing global emissions. Additionally, global emissions of the atmospheric pollutants were carried by monsoon to the high latitude. What is the contribution of it to the Arctic area? Are there any reports concerning the separate contribution of airborne pollutants to land and ocean?

Response: initially, we tried to show Arctic air pollution includes harmful trace gases (e.g. tropospheric ozone) and particles (e.g. black carbon, sulphate) and toxic substances (e.g. polycyclic aromatic hydrocarbons) that can be transported to the Arctic from emission sources located far outside the region, or emitted within the Arctic from activities including shipping, power production, and other industrial activities (**Arnold et al. 2015**). We realized it's not appropriate to put global emissions here with a specific contribution to the Arctic. We will put more references about Arctic air pollutants' transport for better illustration here.

Arnold, S.R., Law, K.S., Brock, C.A., Thomas, J.L., Starkweather, S.M., Salzen, K. von ., Stohl, A., Sharma, S., Lund, M.T., Flanner, M.G., Petäjä, T., Tanimoto, H., Gamble, J., Dibb, J.E., Melamed, M., Johnson, N., Fidel, M., Tynkkynen, V.-P., Baklanov, A., Eckhardt, S., Monks, S.A., Browse, J. and Bozem, H., 2016. Arctic air pollution: Challenges and opportunities for the next decade. *Elem Sci Anth*, 4, p.000104. DOI: <http://doi.org/10.12952/journal.elementa.000104>

2. L46, the reason mercury is key problematic pollutant should be briefly mentioned here. And citation is needed here.

Response: we will add the reference about Hg in Arctic environment here.

L47, what kind of sources are referring here?

Response: the sources could be as the resulting sea ice loss may increase accessibility of the Arctic, leading to increases in air pollutant emissions within the Arctic from activities such as oil and gas extraction or shipping. It is thought that Northern Hemisphere mid-latitude

emissions (from Europe, Asia, and North America) are currently the main source of air pollutants in the Arctic (Stohl, 2006; Sharma et al., 2013), including also toxic contaminants with important atmospheric pathways (e.g. mercury (Hg), certain persistent organic pollutants (POPs)). However, sources of air pollution from within the Arctic or nearby sub-Arctic (defined here as ‘local’) are already important in some regions (Stohl et al. 2013), and these and other sources may grow rapidly in the future (Corbett et al., 2010; Peters et al., 2011). We will revise this part of information.

Shindell D, Faluvegi G. 2009. Climate response to regional radiative forcing during the twentieth century. *Nat Geosci* 4: 294–300. doi: 10.1038/ngeo473.

Stohl A. 2006. Characteristics of atmospheric transport into the Arctic troposphere. *J Geophys Res* 111: D11306. doi: 10.1029/2005JD006888.

Sharma S , Ishizawa M , Chan D , Lavoue D , Andrews E , et al. 2013. 16-Year simulation of Arctic black carbon: Transport, source contribution, and sensitivity analysis on deposition. *J Geophys Res* 118: D017774. doi: 10.1029/2012JD017774.

Stohl A , Klimont Z , Eckhardt S , Kupiainen K , Shevchenko VP , et al. 2013. Black carbon in the Arctic: The underestimated role of gas flaring and residential combustion emissions. *Atmos Chem Phys* 13: 8833–8855. doi: 10.5194/acp-13-8833-2013.

Peters G , Nilssen T , Lindholt L , Eide M , Glomsrød S , et al. 2011. Future emissions from shipping and petroleum activities in the Arctic. *Atmos Chem Phys* 11: 5305–5320. doi: 10.5194/acp-11-5305-2011.

Corbett JJ , Lack DA , Winebrake JJ , Harder S , Silberman JA , et al. 2010. Arctic shipping emissions inventories and future scenarios. *Atmos Chem Phys* 10: 9689–9704. doi: 10.5194/acp-10-9689-2010.

3. L49, “the melting of contaminated ice” in the ocean or also in the terrestrial land?

Response: In here, we meant both melting ice in ocean as well as the melting snow in the terrestrial soils since fluxes from thermokarst rivers would bring the pollutants into the ocean as another source.

4. L68, what is relevant connection between benthic input of metals and air-seawater exchange input?

Response: It has been reported that a large fraction of the organic matter that forms in surface waters in the shelf areas of the Chukchi Sea sinks to the sea floor, which fuels productive benthic communities and causes high rates of sedimentary denitrification (Chang and Devol, 2009; Brown et al., 2015). The Pacific origin water from the Bering Strait is already depleted in nitrate relative to phosphate, and NO_3^- is further depleted relative to PO_4^{3-} in the Chukchi Sea via the effect of sedimentary denitrification (Yamamoto-Kawai et al., 2006). A unique feature of the upper surface water in the western Arctic Ocean is the dominance of a strong, cold

halocline that separates the Pacific-origin surface waters from the underlying Atlantic-origin waters (Aagaard et al., 1981). And metals in deep ocean showed the similar pattern of nutrients (Brown et al., 2015).

Chang, B.X., Devol, A.H., 2009. Seasonal and spatial patterns of sedimentary denitrification rates in the Chukchi sea. *Deep Sea Res.* II 56(17), 1339–1350.

Yamamoto-Kawai, M., Carmack, E., McLaughlin, F., 2006. Nitrogen balance and Arctic through flow. *Nature* 443, 43.

Aagaard, K., Coachman, L.K., Carmack, E., 1981. On the halocline of the Arctic Ocean. *Deep Sea Res.* 28A(6), 529–545.

Brown, Z.W., Casciotti, K.L., Pickart, R.S., Swift, J.H., Arrigo, K.R., 2015. Aspects of the marine nitrogen cycle of the Chukchi Sea shelf and Canada Basin. *Deep Sea Res.* II 118, 73–87.

5. L88-89, the sentence authors make here tried to indicate the inorganic salt ions may increase during the summer melting season, and thence the organic compounds' solubility would change? Now the meaning is not clear. Authors need to rephrase the sentences to clarify.

Response: we will make this sentence clear. We intended to state that inorganic salts are appreciably soluble in organic media, principally of the oxygenated forms (alcohols, ketones, ethers, esters), when they are capable of forming neutral molecules in solution. This property is largely confined to the transition elements. Those of the first long series, and in the trans-actinoid region, accomplish this without forming undebatably covalent compounds; other subgroup elements which are solvent-soluble show a stronger tendency toward covalent bond formation, and may show solubility in chlorinated hydrocarbons and benzenoid solvents in which the first group mentioned are not usually soluble. The salts of the first three groups of the periodic table generally are not organic-soluble, because their co-ordinative power is relatively low, and their solid lattice energies are high.

6. L91, need citation for “the Arctic Ocean is considered as a sink that receives global airborne pollutants”.

Response: we will add the reference source of this sentence.

7. L203, how surface chlorophyll concentrations were calculated or measured?

Response: Spectrophotometry method was used to measure chlorophyll concentrations. It involves the collection of a fairly large water sample, filtration of the sample to concentrate the chlorophyll-containing organisms, mechanical rupturing of the collected cells, and extraction of the chlorophyll from the disrupted cells into the organic solvent acetone. The extract is then analyzed by either a spectrophotometric method (absorbance or fluorescence), using the known optical properties of chlorophyll, or by HPLC. This general method, detailed in Section 10200 H. of Standard Methods, has been shown to be accurate in multiple tests and applications and is the procedure generally accepted for reporting in scientific literature.

8. L218, why H' can be corrected by the salinity? In Fick's law, I am not aware of such connection. H' values are usually considered by the temperature changes.

Response: usually temperature and salinity can be both used to correct Henry laws. However, the salinity of seawater has been indirectly determined by means of electrical conductivity. Since the absolute conductivity cannot be measured as accurately as required for precise salinity measurements (Seitz et al., 2010), the conductivity has been measured relative to that of standard seawater; the conversion to salinity is carried out by means of the (relative) conductivity–salinity relation PSS-78 (JPOTS, 1981a, b). In practice, this is achieved by calibrating salinometers and conductivity–temperature–depth devices using standard seawater, which is diluted to obtain the conductivity of the potassium chloride standard (Culkin, 1986; Bacon et al., 2007) used as a conductivity reference. An unconditional prerequisite for the comparability of salinity measurements over long periods is, therefore, that the salt proportions in standard seawater are stable. Unfortunately, this cannot be guaranteed, as standard seawater is of natural origin.

Seitz, S., Spitzer, P., and Brown, R. J. C.: CCQM-P111 study on traceable determination of practical salinity and mass fraction of major seawater components, *Accredit. Qual. Assur.*, 15, 9–17, <https://doi.org/10.1007/s00769-009-0578-8>, 2010.

Joint Panel on Oceanographic Tables and Standards (JPOTS): Tenth report of the Joint Panel on Oceanographic Tables and Standards – The Practical Salinity Scale 1978 and The International Equation of State of Seawater 1980, *Unesco technical papers in marine science*, 36, 13–17, UNESCO, Paris, France, available at: <http://unesdoc.unesco.org/images/0004/000461/046148eb.pdf>, 1981a.

Joint Panel on Oceanographic Tables and Standards (JPOTS): Background papers and supporting data on the Practical Salinity Scale 1978, *Unesco technical papers in marine science*, 37, UNESCO, Paris, France, available at: <http://unesdoc.unesco.org/images/0004/000479/047932eb.pdf>, 1981b.

Bacon, S., Culkin, F., Higgs, N., and Ridout, P.: IAPSO standard seawater: definition of the uncertainty in the calibration procedure and stability of recent batches, *J. Atmos. Ocean. Tech.*, 24, 1785–1799, <https://doi.org/10.1175/JTECH2081.1>, 2007.

Culkin, F.: Calibration of standard seawater in electrical conductivity, *Sci. Total Environ.*, 49, 1–7, [https://doi.org/10.1016/0048-9697\(86\)90230-5](https://doi.org/10.1016/0048-9697(86)90230-5), 1986.

9. L246, how the uncertainty of air-water exchange net direction was conducted?

Response: we will add this information to the supplementary information. We take the method from Liu et al. (2016).

Liu, Y., Wang, S., McDonough, C. A., Khairy, M., Muir, D., and Lohmann, R.: Estimation of Uncertainty in Air–Water Exchange Flux and Gross Volatilization Loss of PCBs: A Case Study Based on Passive Sampling in the Lower Great Lakes, *Environmental Science & Technology*,

To evaluate the uncertainty in air-water fugacity ratio and the statistically calculated diffusive flux, measured uncertainties of water and air analysis, Henry's law constant, temperature and overall velocity of mass transfer were taken into account. Four variables with random uncertainty of the fugacity ratio was based on Eq. (11) and Eq. (13), of which the uncertainty is shown in Eq. (S1).

$$\delta \ln \left(\frac{f_g}{f_w} \right) = \sqrt{\left(\frac{\delta C_g}{C_g} \right)^2 + \left(\frac{\delta C_w}{C_w} \right)^2 + \left(\frac{\delta H'}{H'} \right)^2 + \left(\frac{\delta T}{T} \right)^2} \quad (\text{S1})$$

The relative standard deviation (RSD) of aqueous and water concentrations $\left(\frac{\delta C_g}{C_g} \right)$ and $\left(\frac{\delta C_w}{C_w} \right)$ are relevant to the analysis. The RSDs of H' was taken value as 50%.

10. L263, why only OH radicals were considered to the degradation of PAHs in the atmosphere?

Response: Dry deposition is more effective than wet deposition as a removal process from the atmosphere. Chemical reactions provide the other main sink for atmospheric PAHs. The gas phase reactions of PAHs with the OH radical, the NO₃ radical and ozone have been widely investigated. Available rate coefficient data are most abundant in the case of the OH radical. The established mechanism of PAH reactions with the OH radical involves the formation of a PAH-OH adduct followed by further reaction with NO₂ or O₃. The observed reaction products include both ring-retaining nitro-PAHs and quinones, as well as ring-opened products such as phthalic acid, phthalaldehyde and phthalic anhydride. The presence of methyl groups in methyl naphthalenes and methyl phenanthrenes in most cases leads to a modest increase in reactivity relative to the parent PAH. For NO₃ reactions, the predominant reaction pathway involves NO₃ addition followed by reaction with NO₂ leading to nitro-PAH formation. The observed rate coefficients are proportional to the nitrogen dioxide concentration. There have been far fewer studies of the gas phase reactions of PAH with ozone.

11. L279-280, Do author have any proofs to support the reason with air trajectories of Russian Arctic?

Response: this reason with air trajectories of Russian Arctic was observed by the previous study (Shevchenko et al. 2003).

V. Shevchenko, A. Lisitzin, A. Vinogradova, R. Stein. Heavy metals in aerosols over the seas of the Russian Arctic. *The Science of the Total Environment* 306 (2003) 11–25.

12. L294, which sea Taymyr Peninsula is closer to? Clarify here. L295, I think Shevchenko et al. 2013 should be moved to previous sentence.

Response: Taymyr Peninsula is close to Kara Sea. We will revise this sentence based on your suggestion.

L419, Can authors explain what molecular weight PAHs were easier to de degraded in the air

because it's important for biocycles to consume these carbon sources by organisms. If most of heavy molecular PAHs enter ocean ecosystem, which may not be consumed by biota.

Response: theoretically, lighter PAHs can be easier degraded. Photo-induced toxicity of PAHs can be driven from formation of intracellular singlet oxygen and other reactive oxygen species (ROS) that cause oxidative damage in biological systems (**El-Alawi et al., 2002**), or formation of photo-products, which exert different, often stronger, bioactivity than the parent compound (**Grote et al., 2005**).

Measurement of short- and long-term toxicity of polycyclic aromatic hydrocarbons using luminescent bacteria. El-Alawi YS, McConkey BJ, George Dixon D, Greenberg BM *Ecotoxicol Environ Saf.* 2002 Jan; 51(1):12-21.

Modeling photoinduced algal toxicity of polycyclic aromatic hydrocarbons. Grote M, Schüürmann G, Altenburger R *Environ Sci Technol.* 2005 Jun 1; 39(11):4141-9.

L440, I suggest authors to put some information of future protective measures for this region.

Response: according to your suggestion, we will add protective measures for the Arctic Ocean in the conclusion part.