Atmosphere–ocean exchange of heavy metals and polycyclic aromatic hydrocarbons in the Russian Arctic Ocean

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10   **Abstract.** Heavy metals and polycyclic aromatic hydrocarbons (PAHs) can greatly influence biotic activities

and organic sources in the ocean. However, fluxes of these compounds as well as their fate, transport, and net

input in the Arctic Ocean have not been thoroughly assessed. During April–November of the 2016 "Russian

High Latitude Expedition", 51 air (gases, aerosols, wet deposition) and water samples were collected from the

Russian Arctic within the Barents Sea, Kara Sea, Leptev Sea, and East Siberian Sea. Here, we report on the

15   Russian Arctic assessment of the occurrence in dry and wet deposition of 35 PAHs and 9 metals (Pb, Cd, Cu,

Zn, Fe, Mn, Ni, and Hg), as well as the atmosphere–ocean fluxes of 35 PAHs and Hg^0. We observed that Hg

was mainly in the gas phase and Pb was most abundant in the gas phase compared with the aerosol and

dissolved water phases. Mn, Fe, Pb, and Zn showed apparently higher levels than the other metals in the three

phases. According to the results for the 35 detected PAHs, the concentrations of PAHs in aerosols and the

20   dissolved water phase were about one magnitude higher than those in gas. The abundances of higher molecular

weight PAHs were highest in the aerosols. Higher levels of both heavy metals and PAHs were observed in the

Barents Sea, Kara Sea, and East Siberian Sea, which were close to areas with urban and industrial sites.

Diagnostic ratios of phenanthrene/anthracene to fluoranthene/pyrene showed a pyrogenic source for the

aerosols and gases, while the patterns for the dissolved water phase were indicative of both petrogenic and

25   pyrogenic sources; pyrogenic sources were most prevalent in the Kara Sea and Leptev Sea. These differences

between air and seawater reflect the different sources of PAHs through atmospheric transport, which included

anthropogenic sources for gases and aerosols and mixtures of anthropogenic and biogenic sources along the

continent in the Russian Arctic. The average dry deposition of $\sum_9$metals and $\sum_{35}$PAHs was 1749 ng m^{-2} d^{-1} and

1108 ng m^{-2} d^{-1}, respectively. The average wet deposition of $\sum_9$metals and $\sum_{35}$PAHs was 33.29 μg m^{-2} d^{-1} and

30   221.31 μg m^{-2} d^{-1}, respectively. For the atmosphere–sea exchange, the monthly atmospheric input of $\sum_{35}$PAHs

was estimated at 1040 tonnes. The monthly atmospheric Hg input was approximately 530 tonnes. These

additional inputs of hazardous compounds may be disturbing the biochemical cycles in the Arctic Ocean.

Key words: Trace metals; PAHs; Russian Arctic; atmosphere–water fluxes

35   **1 Introduction**

The increasing anthropogenic activities associated with growing industries within boundary areas of the Arctic for economic reasons, including hydrocarbon exploration sites and mines in the Russian Arctic, represent potential pollution sources to Arctic ecosystems (Walker et al., 2003;Dahle et al., 2009;Ji et al., 2019). Additionally, the Arctic has long been contaminated by pollutants transported to polar areas from distant

40   locations outside of this region. For example, anthropogenic sources of pollutants in the Arctic have been found to come from the Norilsk industrial area in the Taymyr Peninsula (Reimann et al., 1997;Zhulidov et al., 2011) and from the copper-nickel mining industry in the Kola Peninsula (Boyd et al., 2009;Jaffe et al., 1995). For pollutants transported from outside of the Arctic, reducing global emissions would be an ideal strategy to lessen the impacts of pollutants on Arctic ecosystems. For example, worldwide emissions of mercury will have

45   increased by 25% in 2020 over 2005 levels according to previous estimations (Pacyna et al., 2010), and mercury is a key problematic pollutant in the Arctic. Thus, global emission reductions could help to alleviate problems associated with long-range mercury transport and contamination in the Arctic. In regard to sources close to the Arctic, these may inevitably cause localized ecological risks or risks over a wider regional range. Also of concern is that, with rapid warming of the global climate, the melting of contaminated ice may lead to

50   more pollutant emission into the Arctic Ocean, which could harm its fragile ecosystems.

Pollutants can be transported to the Arctic through both seawater and atmospheric pathways, and the atmospheric pathway is the quickest and most direct way for long-range pollutant transportation, e.g., pollutants can be transported from distant sources to the Arctic within several days or weeks via this pathway (Shevchenko et al., 2003). Reports have revealed that some pollutants such as heavy metals and polycyclic

55   aromatic hydrocarbons (PAHs) can be transported with aerosols over thousands of kilometers to Arctic regions (Rahn and Lowenthal, 1984;Maenhaut et al., 1989;Shaw, 1991;Cheng et al., 1993). Approximately 100 tonnes per year of airborne mercury originating from industrial sources are deposited in the Arctic Ocean (Cone, 2008). While there is evidence that atmospheric inputs make large contributions to the chemical budgets in marine areas, the exact role of these inputs in the Arctic Ocean remains uncertain and may have been previously

60   underestimated (Duce et al., 1991). Numerous studies have proven that aerosol transport is an important way in which atmospheric compounds are transferred from air to ocean water, and this process is susceptible to changes of climate in Arctic regions (Leck et al., 1996;Sirois and Barrie, 1999;Bigg and Leck, 2001). The compounds in aerosols over the Russian Arctic have been reported to show maximal concentrations during the winter/spring season, and 50% of the air pollutants were found to have originated from Russian Arctic pollution

65   itself (Shevchenko et al., 2003). It has also been reported that the natural biodegradation rates of exogenous

compounds in the Arctic Ocean could be lower than those in more temperate oceans such as the Atlantic and Pacific (Bagi et al., 2014). In addition, Vieira et al. (2019) found that some metals (Fe, Mn, and Co) were altered by reductive benthic inputs, and levels were affected by the biological processes of uptake and release in the Arctic Ocean. Because of their toxicity and persistence, high concentrations of heavy metals or other

70   persistent pollutants such as PAHs may disturb the benthic fluxes in cross-shelf mixing in Arctic regions, which could result in adverse effects on marine life, and with the eventual biomagnification in the food web, humans could be affected as well. However, up to now, there has been an insufficient understanding of how these compounds (heavy metals and PAHs) participate in biochemical cycles over the long term in the Arctic Ocean.

The atmosphere–seawater exchange is the major process that controls the residence time and levels of

75   chemical compounds in the Arctic Ocean. In particular, atmospheric deposition is a significant source for pollutants in seawater, and dry deposition in different oceans has been widely studied (Jickells and Baker, 2019;Wang et al., 2019;Park et al., 2019). Although wet deposition (precipitation scavenging) is regarded as playing a predominant role in eliminating pollutants in both gas and particulate phases, current reports on the spatial distribution of pollutants from wet deposition in high-latitude oceans are scarce (Custódio et al., 2014).

80   Moreover, for volatile or semivolatile compounds, the volatilization process is an important pathway for atmosphere–seawater exchanges. Therefore, the atmosphere–water exchange of volatile or semivolatile compounds can be estimated by the net flux of pollutants either volatilizing from seawater to air or depositing from air to seawater (Rasiq et al., 2019;Cheng et al., 2013;Totten et al., 2001). Gonzalez-Gaya et al. (2016) reported on a global assessment of atmosphere–ocean fluxes of 64 PAHs and the net atmospheric PAH input

85   was 0.09 Tg per month to the global ocean. It is undeniable that the atmosphere–seawater exchange rate is greatly influenced by atmospheric temperature variations, and the direction and magnitude of fluxes of compounds between air and seawater vary seasonally (Bamford et al., 1999;Hornbuckle et al., 1994). Additionally, for organic compounds as PAHs, inorganic salt ions can decrease the aqueous solubility of organic compounds (Rasiq et al., 2019). During the period of melting sea ice in the Arctic Ocean, the magnitude and

90   direction of atmosphere–seawater fluxes may be different from those in tropical and subtropical oceans (Gonzalez-Gaya et al., 2016;Rasiq et al., 2019). Although the Arctic Ocean is considered as a sink that receives global airborne pollutants, unfortunately, the characteristics of atmosphere–ocean exchanges of trace metals and organic compounds have remained unclear up to now.

In this study, with the Arctic Ocean as the research area, two categories of pollutants (i.e., 9 heavy metals

95   and 35 PAHs) were measured in aerosols, gas, and seawater, and atmosphere–ocean exchanges of Hg and PAHs were studied. We hypothesized about the relative equilibrium of chemical exchanges between seawater and air

and calculated the net diffusion of atmosphere–ocean exchange of Hg and PAHs in the Arctic Ocean for an evaluation of the double-directional exchange. Meanwhile, the dry and wet deposition of heavy metals and PAHs in the Russian Arctic Ocean were determined. The distributions of heavy metals and PAHs in each sea of

100 the Arctic Ocean and in different phases were also characterized to identify possible sources from the continents.

2 Materials and methods

2.1 Study area and sample collection

All samples were collected during the period of 9th April to 10th November of 2016 as part of the "Russian

105 High Latitude Expedition" carried out on the vessel *Mikhail Somov* (this vessel traveled from the City of Arkhangelsk to Wrangel Island). Fifty-one air and water samples, and eight wet deposition samples were gathered from locations ranging from the southern inlet of the Barents Sea to across the Kara Sea, Laptev Sea, and East Siberian Sea (**Fig. 1**).

2.1.1 Aerosol and gas phase

110 Air samples, including aerosols and concurrent gases as described elsewhere (Reddy et al., 2012), were collected by a high-volume sampler set up at the top of a main rod. A wind vane was connected to the high-volume sampler so that samples could be collected only if the wind was derived from the bow to prevent contamination from ship emissions. The average sampled air volume was 632 m^3 (412–963 m^3) per sample. The aerosols were sampled on Teflon filters (P0325-100EA, Fluoropore, Darmstadt, Germany), and then, the

115 compounds in the gas phase were collected over precleaned polyurethane foams (PUFs). After sampling, the filters and PUFs were placed in polyethylene bags, covered with aluminum foil, and frozen at -20 °C prior to chemical analyses.

2.1.2 Wet deposition and water

Wet deposition samples were collected through a cleaned stainless steel funnel connected to a glass bottle

120 during eight snow events. Water samples were gathered continuously from surface seawater (5 m depth) along the vessel, and these samples were immediately filtered onto borosilicate microfiber glass filters (AP1504700, EMD Millipore, Darmstadt, Germany). Then, the compounds in the dissolved phase were retained on XAD sorbent tubes subjected to controlled flows. The mean filtered water volume was 1239 m^3 (135–2876 m^3). The XAD tubes were stored at 5 °C before their extraction in the laboratory.

2.2 Heavy metal extraction and analysis

For the metal determinations in the aerosol, gas phase, wet deposition, and water samples, Teflon filters, PUFs, and dissolved phases were first Soxhlet-extracted for 8 h by using HNO_3, and then, the samples were diluted with deionized water to 23 mL and subjected to inductively coupled plasma mass spectrometry (ICP-MS) analysis. Specifically, the contents of Pb, Cd, Cu, Co, Zn, Fe, Mn, Ni, and Hg were analyzed on an ICP-MS instrument (Thermo Scientific ICE 3500, Waltham, MA, USA) while making use of rhodium (Rh) as an internal standard. High-resolution (10,000) data were collected to avoid any mass interference problems.

2.3 PAH extraction and analysis

For the PAH determinations in the gas, aerosol, and dissolved phase samples, published procedures were used (Berrojalbiz et al., 2011;Castro-Jimenez et al., 2012;Gonzalez-Gaya et al., 2014). Snow-melt water was extracted by using solid phase HLB Oasis cartridges (60 mg/3 cc) on board. Briefly, cartridges were preconditioned with 5 mL methanol, 10 mL of a mixture of methanol:dichloromethane (1:2), and 10 mL deionized water. Afterward, each sample was combined with a recovery standard and concentrated by N_2 until near dryness. Then, it was eluted with 5 mL hexane, 5 mL of a mixture of hexane:dichloromethane (1:2), and 10 mL deionized water.

Thirty-five PAH species were quantified, including naphthalene, methylnaphthalene (sum of two isomers), 1,4,5-trimethylnaphthalene, 1,2,5,6-tetramethylnaphthalene, acenaphthylene, acenaphthene, fluorene, dibenzothiophene, anthracene, 9-methlyfluorene, 1,7-dimethylfluorene, 9-n-propylfluorene, 2-methyldibenzothiophene, 2,4-dimethyldibenzothiophene, 2,4,7-trimethyldibenzothiophene, 3-methylphenanthrene, 1,6-dimethylphenanthrene, 1,2,9-trimethylphenanthrene, 1,2,6,9-tetramethylphenanthrene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, 3-methylchrysene, 6-ethylchrysene, 1,3,6-trimethylchrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, perylene, dibenzo[*a,h*]anthracene, indeno[*1,2,3-cd*]pyrene, dibenzo[*a,h*]anthracene, and benzo[*g,h,i*]perylene. The PAH quantification was performed with gas chromatography-mass spectrometry (GC-MS). Specifically, we used a gas chromatograph coupled with a triple quadrupole mass selective detector (GS-MS, ITQ 1100, Thermo Scientific, USA) equipped with a DB-5MS chromatographic capillary column (30 m × 0.25 mm i.d. and 0.25-μm film, Agilent Technologies, Santa Clara, CA, USA) operating in electron impact mode (EI) and with selected ion monitoring (SIM) as reported before (Gonzalez-Gaya et al., 2014). The internal standards (anthracene-d_{10}, *p*-terphenyl-d_{14}, pyrene-d_{10}, and benzo[*b*]fluoranthene-d12) were added before operating the GC-MS instrument for the quantification of PAHs, and the recovery of perdeuterated standards (acenaphthene-d_{10}, chrysene-d_{12}, phenanthrene-d_{10}, and perylene-d_{12}) was determined by addition prior to the

procedures of extraction; these values were then used for the correction of measured concentrations.

2.4 Quality assurance and quality control

Analyses of every sample and phase were conducted in the laboratory with field blanks to determine the

analytical limits and recoveries. Breakthroughs of aerosols and gas phases were checked for the Teflon filter

160   and PUF samples. Approximately 90% of the metals and PAHs were obtained during the first half of the sample

analysis, while the remaining 10% were obtained during the second half; for the PAHs, these mostly consisted

of compounds with 2–3 rings. Six blanks (field and laboratory) were collected for the gas phase, while for the

dissolved phase, seven field banks and eight laboratory blanks were used, all of which were extracted along

with the rest of the samples during the analytical procedure. For the gas phase, average $\sum$metal values were

165   approximately 0.049 and 0.052 ng per sample in the field and laboratory blanks, respectively, and average

$\sum$PAH values were approximately 2.44 and 2.06 ng per sample in the field and laboratory blanks, respectively

(**Table S1 and S2, Supplementary material**). For the aerosols, average $\sum$metal values were 0.046 and 0.065

ng per sample in the field and laboratory blanks, respectively, and average $\sum$PAH values were 2.95 and 2.96 ng

per sample in the field and laboratory blanks, respectively. Likewise, for the dissolved phase, values of 0.053

170   and 0.052 ng per sample were obtained for the $\sum$metals and values of 2 and 1.73 ng per sample were obtained

for the $\sum$PAHs. All measured PAHs from field samples exceeded the field and laboratory blank concentrations;

therefore, the quantified compounds were not subtracted by those values. Mean recoveries of perdeuterated

standards used as surrogates in dissolved samples were as follows: 63% for acenaphthene-d_{10}, 54% for

chrysene-d_{12}, 73% for phenanthrene-d_{10}, and 82% for perylene-d_{12}.

175   All concentrations in each medium were corrected by the surrogate recovery for individual samples. The

detection limit was used for the lowest limit of the calibration curve. The quantification limit was equivalent to

the average blank concentration for each phase.

2.5 Data processing

Dry deposition fluxes (F_{DD}, ng m^{-2} d^{-1}) were calculated from field measurements of trace metals and PAHs

180   collected during the expedition over eight time periods. Aerosol deposition fluxes for the metals were

calculated as shown in Eq. (1):

$$F_{DD}(\text{metal}) = C_d V_d \tag{1}$$

where C_d is the concentration of atmospheric aerosols and V_d is the velocity of deposition (m s^{-1}). V_d was

calculated as shown in Eq. (2), and the details have been described elsewhere (Zhang et al., 2001):

185    $$V_d = u_{grav} + \frac{1}{R_a + R_s} \tag{2}$$

where u_{grav} is the gravitational settling velocity and R_a and R_s are the aerodynamic resistance for gaseous

species and the surface resistance, respectively. R_s can be calculated as follows:

$$R_S = \frac{1}{\varepsilon_0 u_*(E_B E_{IM})R_1}$$ (3)

where ε_0 is an empirical constant ($\varepsilon_0 = 3$) and u_* is the friction velocity calculated for gases. E_B is the

190   collection efficiency of Brownian diffusion as a function of the Schmidt number Sc:

$$E_B = (Sc)^{-\gamma}$$ (4)

where γ is an empirical constant ($\gamma = 0.5$). E_{IM} is the collection efficiency from impaction based on the

following formulas (Peters and Eiden, 1992):

$$E_{IM} = (\frac{st}{0.8+st})^2$$ (5)

195   $$st = \frac{V_{grav}V_*^2}{V_a}$$ (6)

where V_a is the kinematic viscosity for air (m^2 s^{-1}). The correction factor (R_1) is the fraction of particles close to

the surface:

$$R_1 = \exp(-st^{1/2})$$ (7)

For PAHs, the specific compound deposition velocity (V_d, cm s^{-1}) was derived from an empirical

200   parameterization (Gonzalez-Gaya et al., 2014):

$$\log(V_d) = -0.261\log(P_L) + 0.387U_{10}Chl_s - 3.082$$ (8)

where P_L is the subcooled liquid vapor pressure of each PAH, U_{10} is the 10 m height wind speed, and CHl_s is

the concentration of surface chlorophyll. With Eq. (8), one can estimate the V_d for each PAH and sampling

period by taking P_L from references and using the field-measured U_{10} and CHl_s. In this study, F_{DD}(PAH) values

205   were estimated by the measured concentrations of the aerosol phase (C_A, ng m^{-3}) by using

$$F_{DD}(PAHs) = 864V_d C_A$$ (9)

where 864 is the unit conversion factor.

The wet deposition fluxes (F_W, ng m^{-3} d^{-1}) of metals/PAHs were estimated by using the quantified

concentrations of metals/PAHs from the collected snow and the precipitated volume of snow-melt water per

210   surface and time period for each of the eight snow events during the expedition.

The air–water diffusive fluxes (F_{AW}, ng m^{-2} d^{-1}) for Hg/PAHs were calculated according to Fick's law:

$$F_{AW} = K_{AW}(\frac{C_G}{H'} - 1000C_{TW})$$ (10)

where C_G and C_{TW} represent the concentration measured in the gas phase (ng m^{-3}) and dissolved phase (ng L^{-1}),

respectively. H' is the temperature dependence of Henry's law constant, and H' values for PAHs were taken

215   from elsewhere (Bamford et al., 1999); H' for Hg was calculated from Eq. (11) for seawater proposed by

Andersson et al. (2008):

$$H' = \exp(\frac{-2404.3}{T} + 6.92) \tag{11}$$

where T is the temperature of the surface water (K). H' was corrected by the field-measured salinity. K_{AW} represents the air–water mass transfer rate (m d^{-1}) calculated by a two-film model (Singh and Xu, 1997) and while considering the nonlinear wind-speed effect. C_{TW} for Hg was calculated with directly measured concentrations, and C_{TW} values for PAHs were calculated by using the measured concentrations in the dissolved phase (C_W) as follows:

$$C_T = \left(\frac{C_W}{1+k_{DOC}DOC}\right) \tag{12}$$

where K_{DOC} was taken as the value of 10% of the octanol–water partitioning coefficient (K_{OW}) (Burkhard, 2000), and DOC represents the dissolved organic carbon (mg L^{-1}).

K_{AW} was calculated by the two-film model:

$$\frac{1}{K_{AW}} = \frac{1}{K_W} \frac{1}{K_A H'} \tag{13}$$

where K_W and K_A are the mass transfer coefficients (m d^{-1}) of Hg and PAHs in the water and air films, respectively. CO_2 in the water phase of the mass transfer coefficient (K_{W,CO_2}, m d^{-1}) can be used to calculate K_W (Gonzalez-Gaya et al., 2016), which is a wind-speed quadratic function at a height of 10 m (U_{10}, m^{-1}) (Nightingale et al., 2000). A Weibull distribution of wind speed was assumed to parameterize K_{W,CO_2} because average wind speeds were used during the sampling period since the gas and dissolved phase concentrations were averaged values for the sampling transects; K_{W,CO_2} was calculated by using a previously reported method (Livingstone and Imboden, 1993):

$$K_{W,CO_2} = 0.24[0.24\eta^2\Gamma\left(1+\frac{2}{\xi}\right) + 0.061\eta\Gamma(1+1/\xi)] \tag{14}$$

where η and ξ are the constants of scale and shape in the Weibull distribution, respectively, and Γ represents a gamma function. $\xi = 2$ (Rayleigh distribution) was used as recommended (Gonzalez-Gaya et al., 2016). η is related to the wind speeds and was calculated with $U_{10} = \eta\Gamma(1 + 1/\xi)$ (Livingstone and Imboden, 1993).

K_W can be calculated by

$$K_W = K_{W,CO_2} \frac{1}{\sqrt{\frac{SC_{PAH}}{600}}} \tag{15}$$

where SC_{PAH} is the Hg/PAH Schmidt number. The same applies for K_A, which was also calculated on the basis of wind speeds and by using the H_2O mass transfer coefficient for the air phase (K_{A,H_2O}, cm s^{-1}):

$$K_{A,H_2O} = 0.2U_{10} + 0.3 \tag{16}$$

$$K_A = 864K_{A,H_2O}\sqrt{\frac{D_{i,a}}{D_{H_2O,a}}} \tag{17}$$

245 where $D_{i,a}$ and $D_{H_2O,a}$ represent the Hg/PAH and H$_2$O diffusive coefficients in air, respectively.

The uncertainty was lower than a factor of one to two in these estimates for metals/PAHs. Most of the increasing uncertainty was associated with the Henry's law constants. The effect of uncertainty on the air–water exchange net direction was assessed by the ratios of air–water fugacity (f_G/f_W) (**Fig. S1 and S2, Supplementary material**), and the findings revealed that most metals and PAHs were not close to the 250 equilibrium of air–water. Among the PAHs, net volatilization was detected only for dibenzothiophene, alkylated phenanthrenes, and fluoranthene.

Gross fluxes of volatilization and absorption depend on the first and second term of Eq. (10). The total accumulated fluxes for the Barents Sea, Kara Sea, Laptev Sea, and East Siberian Sea were acquired by multiplying the mean basin flux with the standard deviation by the surface area of each basin.

255 The estimations of degradation fluxes of PAHs in the atmospheric ocean boundary were calculated as follows:

$$D_{atm} = \frac{(C_{Gf} - C_{Gi})ABL}{t} \tag{18}$$

where C_{Gf} and C_{Gi} are the last concentration after a fixed time in a closed system (ng m^{-3}) and the concentration in the gas phase at the initial time (ng m^{-3}), respectively. t is the time period (average 5 h daytime per day), and ABL represents the average height of the atmospheric boundary layer (380 m). C_{Gf} can be calculated as

$$Ln(\frac{C_{Gi}}{C_{Gf}} = k_{OH}[OH]t \tag{19}$$

where k_{OH} is the rate constant for a PAH reaction with OH radicals (Keyte et al., 2013) and [OH] is the hydroxyl radical concentration in the mixed layer (1000–500 hPa) based on the monthly mean OH radical 265 concentration (Spivakovsky et al., 2000). The mean concentrations of OH were calculated by Eq. (13). The OH concentrations ranged between 5.23 and 17.26 × 10^5 mol cm^{-3}. Besides, only the PAHs in the gas phase were considered while the potential degradation of PAHs bound in aerosols was ignored. Considering the uncertainty of those sources, a relevant error factor of two to three was given in the figure for the degradative fluxes based on the individual PAHs. Because of the large uncertainties in k_{OH} values, the degradation fluxes of PAHs in 270 the atmosphere could not be provided.

3 Results and discussion

3.1 Heavy metals in the atmosphere-ocean

Nine heavy metals were measured, and each metal's average concentration in each sea can be found in

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Table S3. The highest $\sum_9$ metal concentrations in the Barents Sea were found in the gas phase (C_G, ng m^{-3}),

275   where the average concentration was 0.418 ng m^{-3} (**Fig. S3**). The average values of C_G showed no obvious

differences among the four seas, whereas the oceanic area adjacent to the Chukchi Peninsula, Taymyr-Gydan

Peninsula, and Arkhangelsk region showed higher concentrations of the nine metals (**Fig. 2a**). High $\sum_9$ metal

concentrations in the aerosol phase (C_A, ng m^{-3}) were observed in the Barents Sea ($p < 0.05$), where the average

$\sum_9$ metal concentration was 2.713 ng m^{-3} (**Fig. 2b**). These high levels may have been associated with the

280   trajectories of air from the continent of Russia. The distributions of heavy metals in the Russian Arctic Ocean

revealed that the concentrations of the $\sum_9$ metals in seawater were lower than those in air. The average $\sum_9$ metal

concentrations in dissolved water (C_W, ng L^{-1}) ranged from 0.526 to 0.896 µg L^{-1} (Leptev Sea to Barents Sea).

Obviously higher values of C_W were observed in the Barents Sea–Kara Sea region (Yamal Peninsula) and in the

East Siberian Sea (close to Chukchi Peninsula) in comparison to the C_W values in other areas (**Fig. 2c**).

285   The abundance of each metal in gases, aerosols, and dissolved water is dependent on the emission sources.

In this study, Fe and Zn were the most abundant metals detected in aerosols and dissolved water from the

Russian Arctic Ocean, where the average $\sum_9$ metal concentrations in aerosols and dissolved water were 0.64 ng

m^{-3} and 0.91 ng L^{-1}, respectively. Pb was the most abundant metal in the gas phase (the average concentration in

the Russian Arctic Ocean = 0.14 ng m^{-3}). In comparison to aerosols and dissolved water, the gas phase

290   contained higher portions of Hg, which is a finding consistent with the usual form of Hg in the atmosphere

(>98%) and the tendency for the remaining types of Hg to adsorb to particles during atmospheric transport

(Poissant et al., 2008). In all phases, the proportions of Mn, Fe, Pb, and Zn were significantly higher than those

of other heavy metals. Additionally, the metal distributions in the Barents Sea and Kara Sea showed the highest

proportions, followed by the metal distributions in the East Siberian Sea. On the Taymyr Peninsula, there is a

295   mining and metallurgical factory operated by the company Norilsk that processes copper and nickel, and it is

one of the biggest metallurgical factories in the world. This may be a likely source of metals in the Kara Sea

region (Shevchenko et al., 2003). Because of the significant differences in the concentrations of metals in the

marine boundary layer both temporally and spatially throughout the Russian Arctic Ocean (Vinogradova and

Polissar, 1995;Shevchenko et al., 1999), as well as the scarcity of reported data on heavy metals in the

300   atmosphere of this region, it was difficult to compare our data with historical findings. However, our data are

similar to those reported in September of 1993 in the Kara Sea (Rovinsky et al., 1995).

The dry deposition flux that involves aerosols binding to heavy metals (F_{DD}, ng m^{-2} d^{-1}) is a major process

for heavy metal deposition (Shevchenko et al., 2003). In the Russian Arctic Ocean, the average F_{DD} of the $\sum_9$

metals ranged from 392 to 8067 ng m^{-2} d^{-1} (mean = 1792 ng m^{-2} d^{-1}). The largest F_{DD} value was found close to

305   the coast of the East Siberian Sea, where F_{DD} values of Hg and Pb were dominant and values of 305 and 224 ng

m^{-2} d^{-1}, respectively, were observed (**Fig. 3a**). Our results seem to be one magnitude higher than those in the

Red Sea (mean = 615 ng m^{-2} d^{-1}) (Chen et al., 2008) and Mediterranean Sea (mean = 264 ng m^{-2} d^{-1}) (Chester et

al., 1999). However, this comparison may not reflect the strength of the emission sources because dry

deposition is highly dependent on the deposition velocity, which is affected by meteorological conditions such

310   as the humidity, wind speed, and stability of the air column (Mariraj Mohan, 2016). The relative humidity in the

Arctic Ocean tends to be higher in coastal areas and notably we sampled during spring–winter when water

vapor evaporates from the relatively warmer surfaces of seawater (Vihma et al., 2008). Also, the wind over

sampling sites in the Arctic Ocean was approximately 7 m s^{-1} on average (the largest average wind speed was

about 9 m s^{-1} in the Barents Sea), which was significantly higher than the wind in the Red Sea and

315   Mediterranean Sea (0.36–1 m s^{-1}) (Chen et al., 2008;Chester et al., 1999). During the eight snow events

encountered during the expedition, the wet deposition flux of the $\sum_9$ metals (F_{WD}, μg m^{-2} d^{-1}) ranged from 23 to

32 μg m^{-2} d^{-1} (mean = 26 μg m^{-2} d^{-1}) (**Fig. 4a**). Data relevant to the wet deposition flux of heavy metals in the

Arctic region include results for Hg, which was estimated on land in Alaska and the highest deposition was

detected along the southern and southeastern coasts (exceeding 0.05 μg m^{-2} d^{-1}) (Pearson et al., 2019); the

320   values were quite similar to the F_{WD} for Hg in our results (0.05 to 0.09 μg m^{-2} d^{-1}). Through analysis of variance

tests, we did not find any significant difference in the F_{WD} at different locations ($p > 0.05$) for all heavy metals,

while a relatively higher F_{WD} for Hg was observed in coastal areas adjacent to the Taymyr Peninsula with

industrial factories. Pearson et al. (2019) pointed out that there are larger contributions from Hg wet deposition

in the Bering Sea and Gulf of Alaska, which are influenced by the western Pacific downwinds of East Asia,

325   where high Hg emissions from industrial activities and coal burning occur (Wong et al., 2006). The Russian

Arctic Ocean is also affected by Pacific downwinds, which could lead to a combination of heavy metal

deposition from both local anthropogenic sources and long-range transport from Asia. Wet deposition is an

important process for the transfer of heavy metals from gas and aerosol phases to ocean water. Snowfall in the

Arctic is an important fraction of precipitation, but variations in measurements ranging from 20% to 50% can

330   occur during windy conditions even with sampling equipment designed with wind protection (Rasmussen et al.,

2012). However, snow events are quite sporadic in the Russian Arctic Ocean during spring–summer compared

with the other deposition processes. Nevertheless, the wet deposition in our study has relatively high

uncertainty and is under regional influences.

        For many heavy metals that form volatile species, there is additional evidence that their existence in water

335   is strongly related to releases from terrestrial environments rather than internal cycling in aquatic systems

(Robert, 2013). For example, following the deposition of atmospheric Fe, a non-volatile species, the concentrations in water are influenced mainly by the particulate phase and its dissolution, whereas for Hg, a volatile species that predominantly exists in the atmosphere as a gas (Hg^0), the concentrations of volatile Hg species in water are largely influenced by volatilization and deposition processes at the air–water interface;

340 portions of the Hg in aquatic systems ends up being converted to methylmercury (Mason and Sheu, 2002;Sunderland and Mason, 2007;Selin et al., 2007;Strode et al., 2007). Hg concentrations in the gas phase in the present study were significantly lower than those measured in 1996 in the Northern Hemisphere (1.5–1.7 ng m^{-3}) and Southern Hemisphere (1.2–1.3 ng m^{-3}) (Steffen et al., 2005;Slemr et al., 2003;Wängberg et al., 2007;Kim et al., 2005). Steffen et al. (2002) indicated that there has been increasing retention of Hg in the

345 Arctic region based on analyses of long-term measurements of atmospheric Hg concentrations. Diffusive air–water exchange is the dominant process driving the exchange of Hg in the ocean. The net diffusive air–water exchange (F_{AW}, ng m^{-2} d^{-1}) was estimated by a two-film resistance model (Robert, 2013). The net input of Hg was calculated as shown in **Fig. 3b**, and the results revealed there was a net input from the atmosphere to the ocean at all stations, especially for the stations close to industrial/urban areas. The integrated

350 monthly F_{AW} fluxes (tonnes per month) for Hg were of the same order of magnitude as the F_{DD} fluxes for Hg and other heavy metals in the Russian Arctic Ocean (**Fig. S4**). For Hg, the gross volatilization and gross absorption in the Russian Arctic Ocean were 250 tonnes per month and 530 tonnes per month, respectively. In consideration of previous studies concerning atmospheric mercury depletion events (AMDEs) during which the net input of Hg in the Arctic was evaluated (Brooks et al., 2006;Lindberg et al., 2001), we adjusted our

355 sampling times to avoid sampling during sunrise when the autocatalytic release of sea salt aerosols changes the oxidative photochemistry in the stratified planetary boundary layer where elemental and reactive Hg in the gas phase is oxidized by reactive halogens. It was estimated that about 99 to 496 tonnes of Hg are deposited per year in the Arctic during AMDEs (Skov et al., 2006;Ariya et al., 2004). The net input of Hg in this study was apparently one order of magnitude higher than that caused by the AMDEs, and this discrepancy may have been

360 related to the fact that the previous studies were estimated based on the terrestrial boundary between air masses and snowpack, and that the different locations and seasons were affected by different meteorological conditions. In northern regions it has been shown that Hg undergoes long-range transport from Eurasia, especially during the winter season (Poissant et al., 2008). These net amounts of Hg entering into the Arctic Ocean pose potential risks to marine biota because Hg is poorly mobile and can be retained by aquatic biota that are exposed to the

365 Hg during the deposition process (Harris et al., 2007).

3.2 PAHs in the atmosphere-ocean

Thirty-five individual PAHs, which included isomer groups such as alkylated PAHs, were measured. The average concentrations of PAHs in each sea of the Russian Arctic Ocean are shown in **Table S4**. The average values of C_G showed no obvious differences in the Kara Sea, Laptev Sea, and East Siberian Sea ($p > 0.05$), and

370 no particularly high levels of C_G were detected at all of the sampling sites (**Fig. 5a**). The highest $\sum_{35}$ PAH concentration in the gas phase (C_G, ng m^{-3}) occurred in the Barents Sea, and the value was 215 ng m^{-3}. PAH concentrations in aerosols (C_A, ng m^{-3}) in the Barents Sea, Kara Sea, and East Siberian Sea were apparently higher than those in the gas phase (**Fig. 5b**) with average C_A values of 215.67, 130.80, and 77.72 ng m^{-3}, respectively. Similar to the pattern for heavy metals mentioned above, these chemicals may have been derived

375 from atmospheric transport from the Russian continent. The average $\sum_{35}$ PAH concentrations in dissolved water (C_W, ng L^{-1}) ranged from 13.12 ng L^{-1} (Laptev Sea) to 60.88 ng L^{-1} (Barents Sea), of which the variability was similar to that of PAH concentrations in aerosols. Higher levels of C_W were also found along the coast of the Yamal-Gydan Peninsula where petrol and natural gas industries have active sites (**Fig. 5c**).

The contribution of each PAH in the gas, aerosol, and dissolved water phases is determined by its source,

380 volatility, and hydrophobicity (Lima et al., 2005). The low-molecular weight PAHs were dominant in gas and dissolved water (**Fig. S5**). In the gas phase, low-molecular weight PAHs occupied more than 75% of the $\sum_{35}$ PAHs, which mainly contained methylated phenanthrenes, e.g., methylphenanthrene (mean = 1.31 ng m^{-3}), dimethylphenanthrene (mean = 1.27 ng m^{-3}), and trimethylphenanthrene (mean = 1.32 ng m^{-3}), and methylated dibenzothiophenes, e.g., methyldibenzothiophene (mean = 1.29 ng m^{-3}), dimethyldibenzothiophene (mean =

385 1.27 ng m^{-3}), and trimethyldibenzothiophene (mean = 1.32 ng m^{-3}). In dissolved water, methylnapthalene and tetramethylnaphthalene were the most abundant PAHs with average concentrations of 1.12 and 1.45 ng L^{-1}, respectively. Measured values of C_G, C_A, and C_W are known to vary with the changes of each PAH concentration in the marine environment (Berrojalbiz et al., 2011;Castro-Jimenez et al., 2012;Cabrerizo et al., 2014). However, there were no previous reports about the occurrence of PAHs in the Russian Arctic atmosphere

390 and ocean.

The average dry deposition flux (F_{DD}) of the $\sum_{35}$ PAHs was 1108 ng m^{-2} d^{-1}. Dry deposition is a major process for high-molecular weight PAHs bound to aerosols (**Fig. 6a**). The deposition values varied mainly in accordance with the PAH concentrations of aerosols in suspension and the factors influencing the deposition velocities (wind speed, compound vapor pressure, etc.). The wet deposition flux of the $\sum_{35}$ PAHs (F_{WD}, ng m^{-2}

395 d^{-1}) ranged from 205 to 241 µg m^{-2} d^{-1}. Wet deposition is an important purging process for semivolatile organic compounds such as PAHs in the gas and aerosol phase. Snow events are quite sporadic in the Arctic Ocean, and thus, these have lower relevance for wet deposition of PAHs in this region.

The estimated net diffusion of air–water exchange (F_{AW}, ng m^{-2} d^{-1}) revealed that most PAHs had net inputs from the atmosphere to ocean except for the more volatile PAHs such as 2–3 ring PAHs (**Fig. 6b**). This is

400   consistent with previous reports in which the results showed that diffusion during air–water exchange is the main process for transfers of relatively lighter volatile organic compounds in the marine environment (Castro-Jimenez et al., 2012;Jurado et al., 2005). The integrated monthly F_{AW} fluxes (tonnes per month) of 5–6 ring PAHs were comparable to F_{DD} fluxes in the Russian Arctic Ocean, whereas only the East Siberian Sea showed higher levels of dry deposition (**Fig. S6**). In all of the four seas, the F_{AW} fluxes of 3–4 ring PAHs were

405   at the same magnitude as the F_{DD} fluxes. The total volatilization and total adsorption of the $\sum_{35}$ PAHs in the Russian Arctic Ocean amounted to 2600 tonnes per month and 3640 tonnes per month, respectively, and thus, there was a net input of the $\sum_{35}$ PAHs from the atmosphere to marine environment that reached 3276 tonnes, which was 100 times higher than the aerosol-bound $\sum_{35}$ PAHs that underwent dry deposition (estimated at around 30 tonnes per month). In other reports, Gonzalez-Gaya et al. (2016) estimated the global input of PAHs

410   from the atmosphere to ocean to be on the order of 90,000 tonnes per month and Reddy et al. (2012) reported that the input of PAHs to the ocean in the Gulf of Mexico in 2010 after the enormous Deepwater Horizon oil spill was 20,000 tonnes. Such comparisons suggest that the diffusive fluxes in the Russian Arctic Ocean play an important role in the atmosphere–ocean exchange of PAHs, whereas there is a relatively lower input of PAHs to the Russian Arctic Ocean on the global scale.

415   In addition to the transfers of PAHs to the ocean, PAHs also can be degraded during transport through the atmosphere because of reactions with OH radicals (Keyte et al., 2013). The degradation fluxes (D_{atm}, ng m^{-2} d^{-1}) of PAHs in the gas phase of the oceanic atmosphere (**Fig. 7**) was estimated at 3000 tonnes per month for the $\sum_{35}$ PAHs, and this represents an additional PAH sink (see Methods). In general, the large amounts of PAHs undergoing net deposition to the ocean and degradation during atmospheric transport must be indicative of large

420   source areas in the Russian Arctic. Notably, PAHs have been increasing in the atmosphere owing to wildfires and fossil fuel use over the past century (Zhang and Tao, 2009). The high-molecular weight PAHs were dominant in the aerosols (**Fig. 5**) originating from pyrolytic sources (Lima et al., 2005). Besides, high abundances of alkylated PAHs were observed in the gas and dissolved phases, and along with the evaluations of the diagnostic ratios (**Fig. S7**), the results were suggestive of pyrogenic sources for PAHs in gases and aerosols,

425   and mixtures of pyrogenic and petrogenic sources for PAHs in dissolved water (mostly for the Leptev Sea and East Siberian Sea). Other sources contributing to the occurrence of PAHs may have involved both anthropogenic and biogenic sources on the land (Cabrerizo et al., 2011). In this region, it can be assumed that PAHs in the atmosphere (gas and aerosol) originated from anthropogenic sources including industrial and urban

430 activities, while PAHs in the seawater at the sites with relatively less anthropogenic sources, i.e., the Leptev Sea and East Siberian Sea, originated from a mixture of anthropogenic and biogenic sources. This indicates that atmospheric transport of PAHs derived from anthropogenic activities is the main input pathway for the Arctic Ocean.

Because PAHs are toxic, these chemicals can have an adverse influence on food webs in marine ecosystems (Hylland, 2006). In particular, even though PAHs are present at natural background levels in the

435 marine environment, the massive usage of fossil fuels has led to increases in PAH emissions and excessive PAH concentrations in many marine environments. The present study indicates that are high contributions of diffusive atmospheric PAHs to the Arctic Ocean, and these chemicals are potentially perturbing the carbon cycle in the ocean and posing risks to the fragile Arctic marine food webs. Thus, further studies of the impacts of such chemicals are warranted.

440 **4 Conclusion**

This study presents the occurrence and atmosphere–ocean fluxes of 35 PAHs and 9 heavy metals in the Arctic Ocean. Dry deposition and wet deposition fluxes of nine heavy metals in aerosols were estimated at 2205 ng m^{-2} d^{-1} and 10.95 μg m^{-2} d^{-1}, respectively. The net gross absorption of Hg in the Arctic Ocean was estimated at 280 tonnes per month. A net input of PAHs from the atmosphere to the Arctic Ocean was observed

445 for most of the PAHs (35 species), especially for the low-molecular weight PAHs. The net atmospheric input of the 35 PAHs was estimated at 3276 tonnes per month. The current occurrences of semivolatile aromatic hydrocarbons could have been derived from biogenic sources and anthropogenic sources from continental land masses, especially for the locations close to industrial areas. These input concentrations of Hg and PAHs sources may be causing adverse effects on the fragile Arctic marine ecosystems, and this issue warrants further

450 research.

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Figure caption list

Figure 1. Locations of investigated islands for soil sampling and trajectory of the vessel in the Russian Arctic.

Figure 2. Occurrence of heavy metals. Results show the concentrations of heavy metals in the **(a)** gas phase, **(b)** aerosol phase, **(c)** and dissolved water phase. Colored bars show the sum of nine quantified metals. The number at the bottom of the legend bars represent the concentration scale as same as Figure 3-7.

Figure 3. Measured atmosphere–ocean exchange of heavy metals. **(a)** Fluxes of dry deposition for nine heavy metals; **(b)** fluxes of net diffusive air–water exchange for Hg. In panel **(a)**, colored bars represent the sum of nine heavy metals. In panel **(b)**, downward bars represent the net deposition into the ocean, and upward bars represent the net volatilization of Hg.

Figure 4. Wet deposition of **(a)** heavy metals and **(b)** PAH fluxes. The measured wet deposition of heavy metals and PAHs occurred during the eight snow events encountered during the vessel expedition.

Figure 5. Occurrence of PAHs in the Russian Arctic Ocean. Concentrations of PAHs in the **(a)** gas phase, **(b)** aerosol phase, and **(c)** dissolved water phase. Color bars indicate the sum of 35 PAHs, where each PAH corresponds to the bottom legend (colors range from red for the heaviest molecular weight PAHs to green for the lightest molecular weight PAHs).

Figure 6. Measured atmosphere–ocean exchange of PAHs. **(a)** Dry deposition fluxes for the 35 measured PAHs; **(b)** net diffusive air–water exchange fluxes (all net deposition into the ocean) for fluoranthene, tetramethylphenanthrene, trimethylphenanthrene, and dibenzothiophene. Color bars indicate the sum of the 35 quantified compounds, and each color represents the individual PAHs in the bottom legend (colors range from red for the heaviest molecular weight PAHs to green for the lightest molecular weight PAHs).

Figure 7. Atmospheric degradation of PAHs. Estimated fluxes of degraded PAHs in the gas phase following reaction with OH radicals.
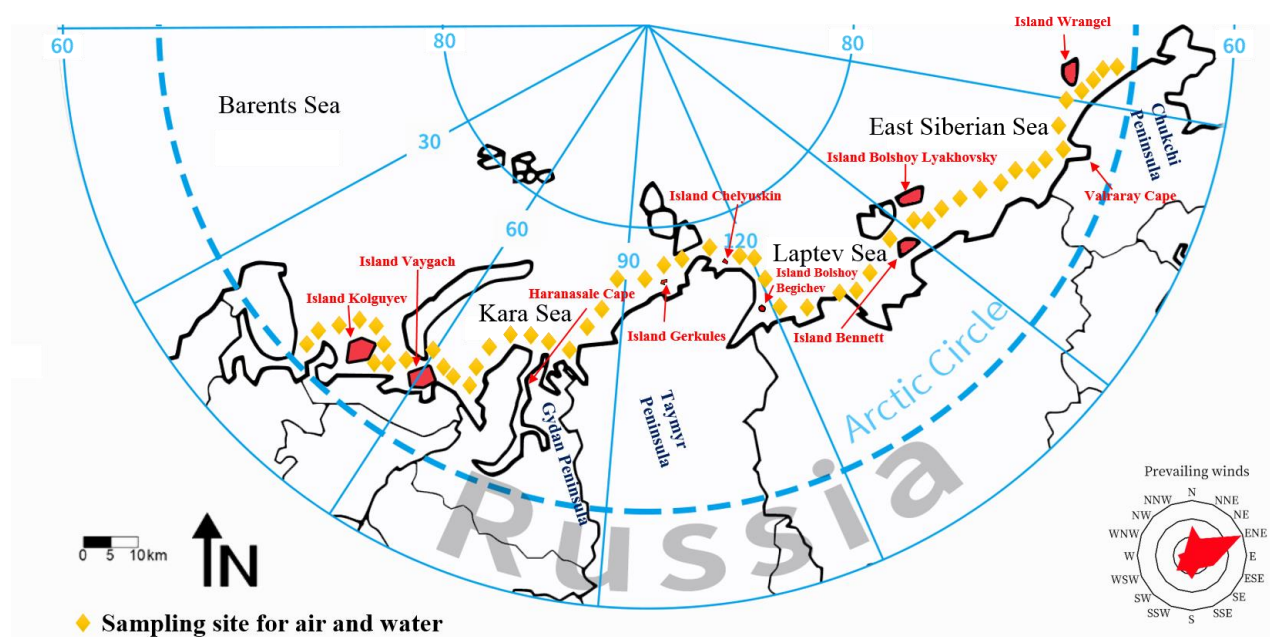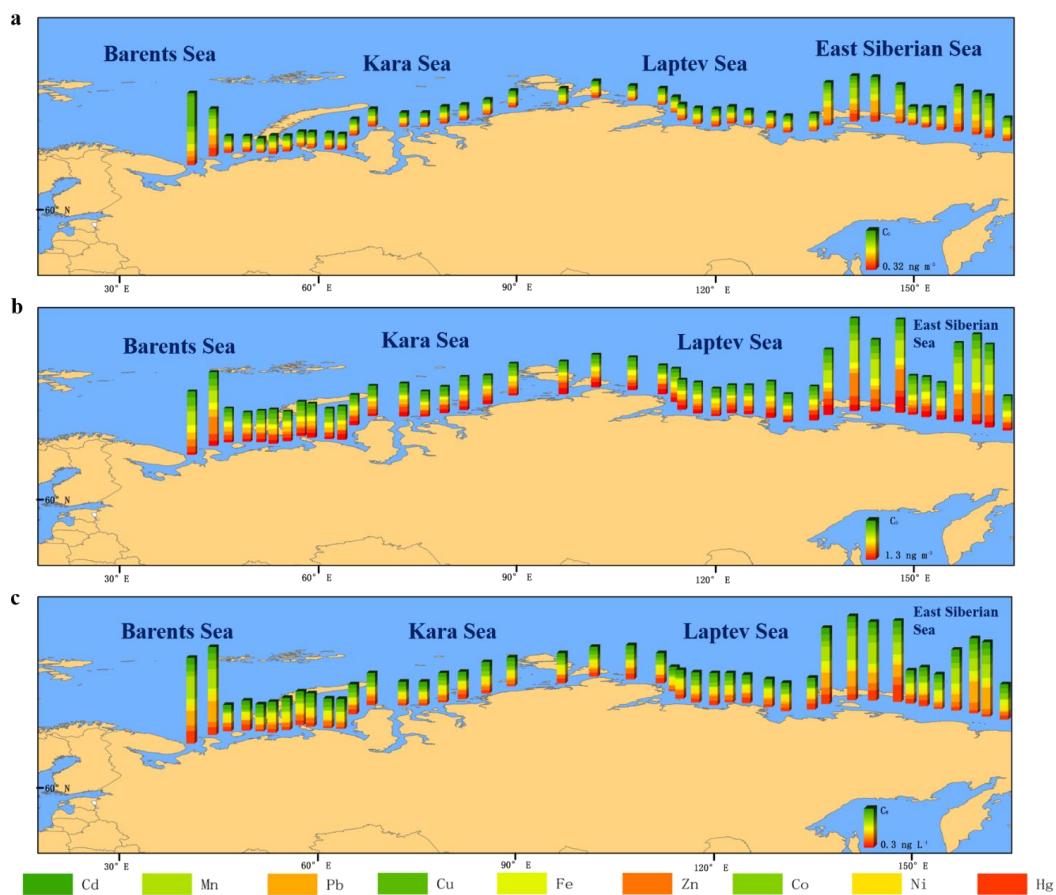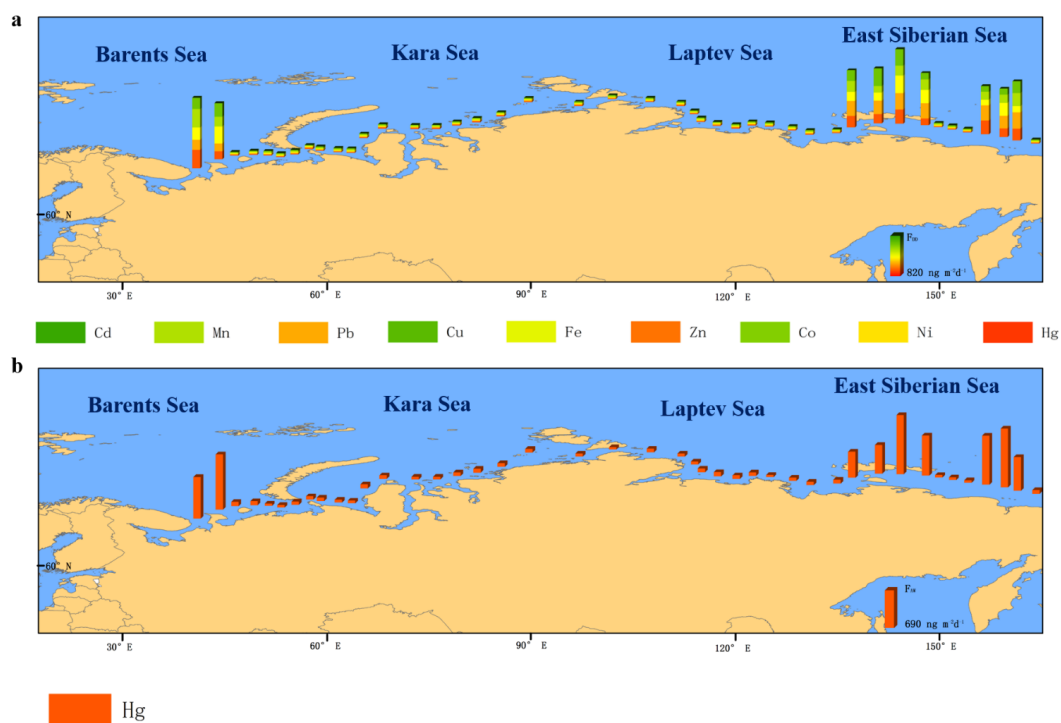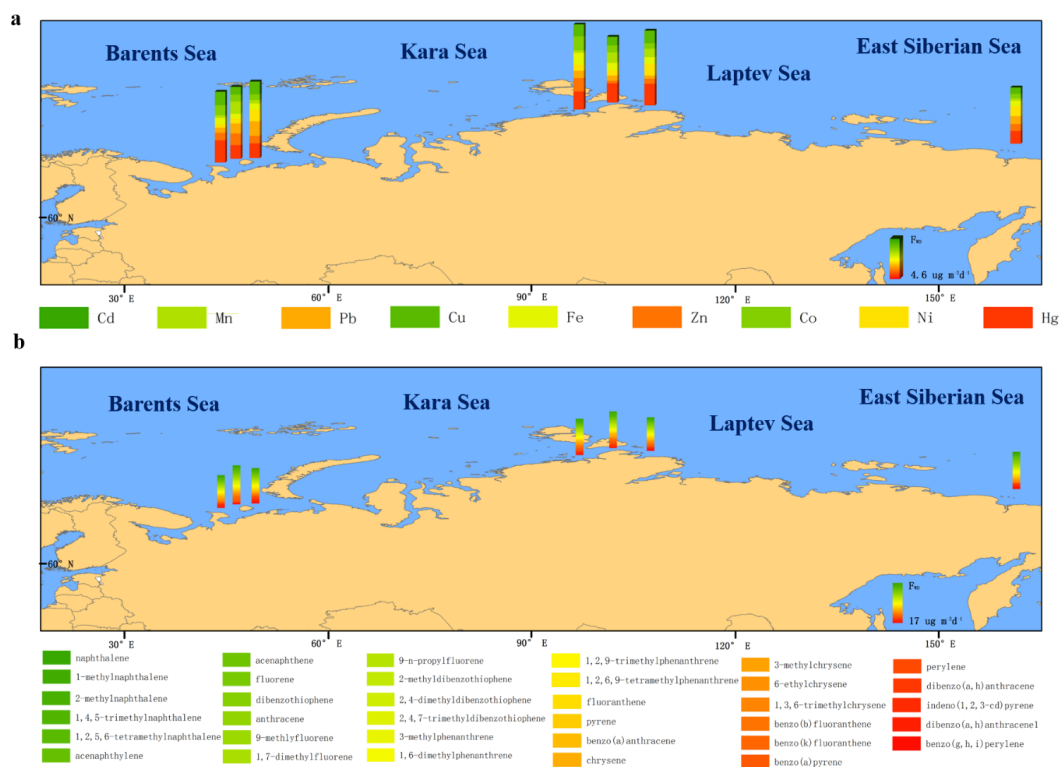
Figure 1.

Figure 2.

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Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.