Supplementary Material

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

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Figure number: 7

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Table S1. Mean concentrations of heavy metals in gas, aerosol, and dissolved phase blanks.

	Gas phase		Aerosol phase		Dissolved phase	
	Field blank (total ng)	Laboratory blank (total ng)	Field blank (total ng)	Laboratory blank (total ng)	Field blank (total ng)	Laboratory blank (total ng)
Cd	0.010	0.005	0.002	0.009	0.004	0.006
Cu	0.008	0.009	0.002	0.008	0.009	0.004
Co	0.002	0.009	0.009	0.001	0.003	0.005
Mn	0.005	0.005	0.009	0.009	0.006	0.007
Fe	0.009	0.003	0.004	0.006	0.005	0.009
Ni	0.002	0.003	0.009	0.007	0.010	0.002
Pb	0.002	0.009	0.007	0.010	0.006	0.007
Zn	0.008	0.005	0.003	0.006	0.004	0.004
Hg	0.049	0.002	0.001	0.009	0.006	0.009
$\sum_{metals}$	**0.049**	**0.052**	**0.046**	**0.065**	**0.053**	**0.052**

Table S2. Mean concentrations of PAHs in gas, aerosol, and dissolved phase blanks.

	Gas phase		Aerosol phase		Dissolved phase	
	Field blank (total ng)	Laboratory blank (total ng)	Field blank (total ng)	Laboratory blank (total ng)	Field blank (total ng)	Laboratory blank (total ng)
Naphthalene	0.20	0.17	0.11	0.08	0.09	0.05
1-methylnaphthalene	0.12	0.17	0.03	0.04	0.01	0.00
2-methylnaphthalene	0.10	0.05	0.09	0.10	0.12	0.10
1,4,5-trimethylnaphthalene	0.16	0.13	0.20	0.07	0.02	0.15
1,2,5,6-tetramethylnaphthalene	0.20	0.14	0.01	0.08	0.00	0.09
Acenaphthylene	0.13	0.03	0.05	0.15	0.11	0.13
Acenaphthene	0.13	0.13	0.03	0.18	0.04	0.15
Fluorene	0.19	0.08	0.10	0.10	0.21	0.21
Dibenzothiophene	0.01	0.06	0.02	0.03	0.13	0.09
Anthracene	0.06	0.16	0.00	0.19	0.12	0.10
9-methlyfluorene	0.20	0.16	0.13	0.08	0.07	0.07
1,7-dimethylfluorene	0.18	0.16	0.04	0.02	0.12	0.02
9-n-propylfluorene	0.14	0.13	0.12	0.00	0.10	0.07
2-methyldibenzothiophene	0.03	0.10	0.05	0.04	0.04	0.17
2,4-dimethyldibenzothiophene	0.13	0.18	0.04	0.03	0.00	0.06
2,4,7-trimethyldibenzothiophene	0.09	0.00	0.18	0.13	0.12	0.13
3-methylphenanthrene	0.06	0.09	0.09	0.05	0.07	0.08
1,6-dimethylphenanthrene	0.12	0.09	0.17	0.06	0.12	0.01
1,2,9-trimethylphenanthrene	0.21	0.15	0.04	0.11	0.21	0.19
1,2,6,9-tetramethylphenanthrene	0.10	0.06	0.03	0.20	0.15	0.04
Fluoranthene	0.20	0.04	0.14	0.03	0.20	0.02
Pyrene	0.09	0.15	0.04	0.07	0.15	0.06
Benzo[a]anthracene	0.01	0.13	0.05	0.02	0.03	0.01
Chrysene	0.04	0.05	0.05	0.18	0.14	0.05
3-methylchrysene	0.15	0.14	0.09	0.16	0.11	0.11
∑PAHs	**2.83**	**2.61**	**1.78**	**2.14**	**2.38**	**2.12**

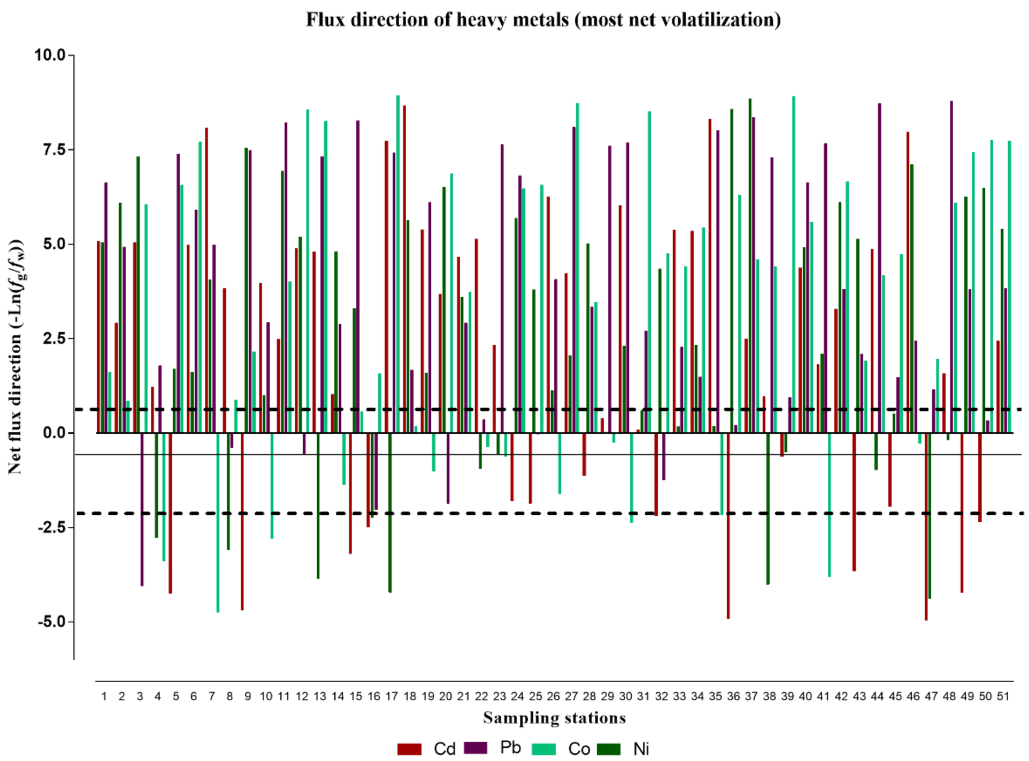
Table S3. Mean concentrations of heavy metals per sea for each measured matrix.

	Gas Phase (ng m^{-3})				Aerosol Phase (ng m^{-3})				Dissolved Phase (ng L^{-1})			
	Barents Sea	Kara Sea	Leptev Sea	East Siberian Sea	Barents Sea	Kara Sea	Leptev Sea	East Siberian Sea	Barents Sea	Kara Sea	Leptev Sea	East Siberian Sea
Cd	0.003	0.003	0.002	0.003	0.014	0.013	0.011	0.013	0.004	0.003	0.003	0.003
Cu	0.001	0.001	0.001	0.001	0.023	0.018	0.014	0.017	0.006	0.005	0.004	0.005
Co	0.001	0.001	0.001	0.001	0.008	0.006	0.003	0.005	0.002	0.001	0.001	0.001
Mn	0.061	0.042	0.005	0.031	0.432	0.278	0.035	0.131	0.093	0.063	0.008	0.053
Fe	0.065	0.054	0.040	0.044	1.325	1.066	0.836	0.909	0.335	0.268	0.176	0.230
Ni	0.006	0.006	0.007	0.007	0.030	0.032	0.033	0.035	0.007	0.008	0.008	0.009
Pb	0.194	0.209	0.055	0.112	0.188	0.137	0.033	0.068	0.053	0.029	0.008	0.028
Zn	0.083	0.080	0.066	0.076	1.688	1.392	1.296	1.392	0.395	0.403	0.317	0.358
Hg	0.004	0.005	0.003	0.005	0.005	0.004	0.003	0.003	0.001	0.001	0.001	0.001
$\sum_{metals}$	**0.418**	**0.401**	**0.18**	**0.28**	**3.713**	**2.946**	**2.264**	**2.573**	**0.896**	**0.781**	**0.526**	**0.688**

Table S4. Mean concentrations of PAHs per sea for each measured matrix.

	Gas Phase (ng m^{-3})				Aerosol Phase (ng m^{-3})				Dissolved Phase (ng L^{-1})			
	Barents Sea	Kara Sea	Leptev Sea	East Siberian Sea	Barents Sea	Kara Sea	Leptev Sea	East Siberian Sea	Barents Sea	Kara Sea	Leptev Sea	East Siberian Sea
Naphthalene	0.634	0.576	0.450	0.511	6.015	3.185	0.493	2.062	4.103	3.559	0.808	2.077
1-methylnaphthalene	0.550	0.587	0.615	0.522	5.739	3.877	0.442	1.536	3.993	3.384	0.868	1.880
2-methylnaphthalene	0.566	0.407	0.587	0.574	3.970	3.964	0.596	1.515	4.633	2.457	0.820	2.334
1,4,5-trimethylnaphthalene	0.449	0.630	0.655	0.565	5.911	3.426	0.481	1.360	5.164	3.376	0.794	2.350
1,2,5,6-tetramethylnaphthalene	0.571	0.616	0.500	0.612	6.068	3.782	0.423	1.801	4.899	3.141	0.722	2.305
Acenaphthylene	0.539	0.599	0.568	0.584	6.743	3.990	0.570	1.394	3.470	3.035	0.824	2.246
Acenaphthene	0.596	0.597	0.531	0.538	5.506	2.890	0.571	2.207	4.120	3.021	0.791	1.781
Fluorene	1.251	1.396	1.338	1.265	5.496	3.657	0.439	1.298	4.334	3.127	0.755	2.520
Dibenzothiophene	1.281	1.323	1.301	1.257	6.062	2.967	0.474	0.746	2.208	1.473	0.529	1.913
Anthracene	1.309	1.345	1.348	1.323	6.712	3.346	0.378	1.635	1.908	1.783	0.499	1.370
9-methlyfluorene	1.368	1.280	1.313	1.249	5.588	3.195	0.529	1.505	2.006	1.670	0.512	1.826
1,7-dimethylfluorene	1.322	1.307	1.274	1.323	4.782	3.574	0.440	1.203	1.585	1.461	0.469	1.745
9-n-propylfluorene	1.254	1.269	1.216	1.276	4.719	2.838	0.498	1.626	1.795	1.373	0.659	1.759
2-methyldibenzothiophene	1.276	1.384	1.261	1.244	5.447	3.101	0.515	2.053	1.583	1.397	0.423	1.742
2,4-dimethyldibenzothiophene	1.306	1.317	1.267	1.193	4.874	2.601	0.562	1.856	2.298	1.261	0.525	1.519
2,4,7-trimethyldibenzothiophene	1.278	1.379	1.309	1.313	6.458	4.140	0.375	1.840	2.293	1.405	0.439	1.557
3-methylphenanthrene	1.328	1.348	1.300	1.281	7.181	3.332	0.494	1.135	2.298	1.475	0.479	1.760
1,6-dimethylphenanthrene	1.235	1.297	1.255	1.296	5.046	2.582	0.556	1.703	1.769	1.127	0.632	1.536
1,2,9-trimethylphenanthrene	1.349	1.319	1.305	1.290	6.174	2.545	0.555	0.725	2.290	1.241	0.464	1.712
1,2,6,9-tetramethylphenanthrene	1.345	1.275	1.296	1.257	7.042	3.705	0.635	1.628	1.629	1.046	0.597	1.795
Fluoranthene	0.006	0.006	0.006	0.005	4.530	2.511	0.453	1.212	2.075	1.358	0.442	1.766
Pyrene	0.004	0.006	0.005	0.005	6.937	3.952	1.170	2.919	0.032	0.019	0.005	0.021

Benzo[a]anthracene	0.006	0.006	0.005	0.006	6.990	4.575	1.052	3.070	0.027	0.020	0.004	0.013
Chrysene	0.005	0.004	0.005	0.005	7.266	4.899	1.126	3.410	0.036	0.011	0.004	0.013
3-methylchrysene	0.005	0.004	0.005	0.005	7.504	4.636	0.902	3.084	0.026	0.021	0.005	0.017
Naphthalene	0.005	0.005	0.006	0.004	6.564	4.976	1.019	3.311	0.032	0.020	0.006	0.014
1-methylnaphthalene	0.006	0.003	0.005	0.005	6.544	4.323	0.998	3.573	0.034	0.026	0.005	0.015
2-methylnaphthalene	0.005	0.005	0.006	0.005	6.801	4.156	1.066	3.265	0.024	0.025	0.006	0.017
1,4,5-trimethylnaphthalene	0.005	0.006	0.006	0.005	6.546	3.801	0.992	3.185	0.028	0.025	0.005	0.014
1,2,5,6-tetramethylnaphthalene	0.004	0.004	0.005	0.004	6.763	4.376	1.096	3.726	0.037	0.020	0.004	0.012
Acenaphthylene	0.005	0.006	0.005	0.005	6.590	4.219	1.084	2.986	0.042	0.023	0.004	0.017
Acenaphthene	0.005	0.005	0.004	0.004	7.233	4.721	1.117	2.945	0.029	0.026	0.005	0.014
Fluorene	0.005	0.006	0.005	0.005	6.879	4.611	1.019	3.507	0.029	0.015	0.004	0.014
Dibenzothiophene	0.004	0.006	0.005	0.004	6.725	4.100	1.058	3.402	0.033	0.019	0.007	0.007
Anthracene	0.006	0.005	0.005	0.006	6.270	4.340	0.852	3.298	0.024	4.021	0.005	0.010
$\sum_{35}$PAHs	**20.88**	**21.32**	**20.76**	**20.54**	**215.67**	**130.80**	**25.03**	**77.72**	**60.88**	**47.46**	**13.12**	**39.69**



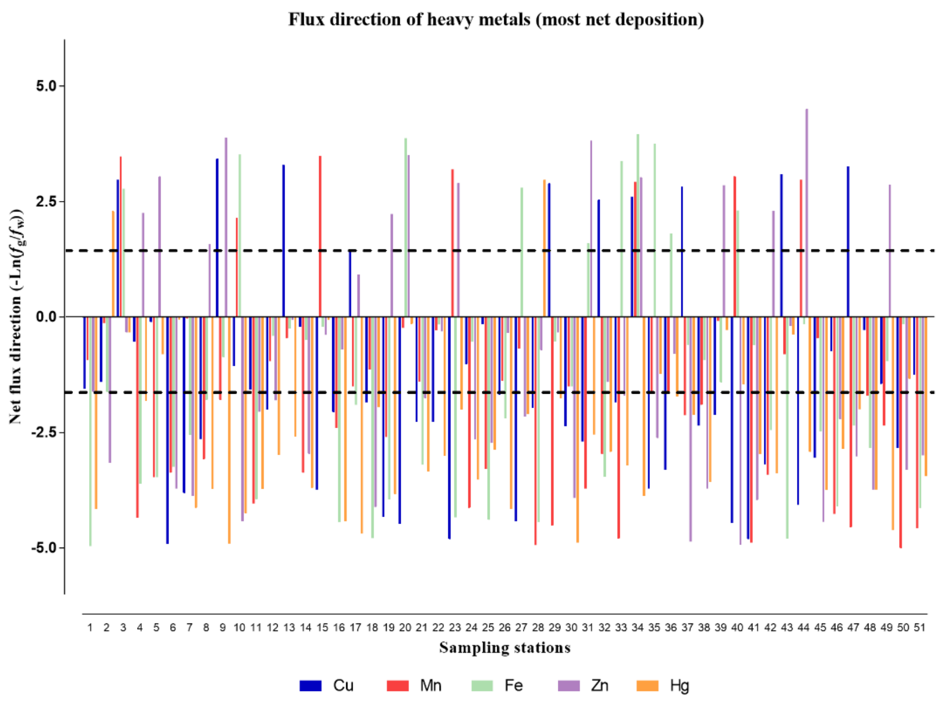


Figure S1. Uncertainty of the net direction of air-water diffusive fluxes. Estimated fugacity ratio of air to water (f_g/f_w) for heavy metals for individual sampling stations. A factor of three of maximum uncertainty is considered. The chemical approaches air equilibrium when -Ln (f_g/f_w) range between 1.3 and -1.5. If -Ln (f_g/f_w)>1.3 or -Ln (f_g/f_w)<-1.5, a net deposition or net volatilization of each heavy metal occurs at the station, respectively

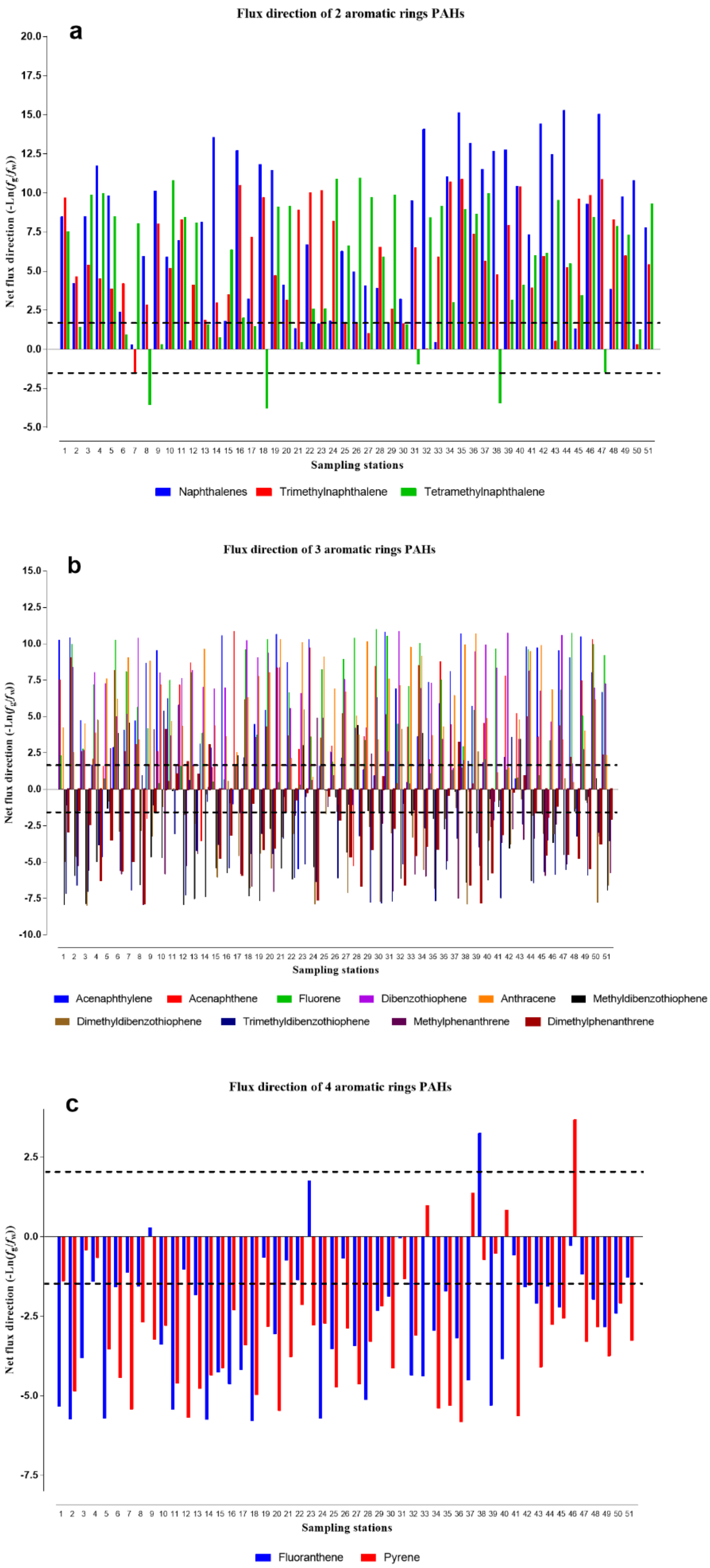


Figure S2. Uncertainty of the net direction of air-water diffusive fluxes. Estimated fugacity ratio of air to water (f_g/f_w) for 2 aromatic rings PAHs (a), 3 aromatic rings PAHs (b), 4 aromatic rings PAHs (c) for individual sampling stations. A factor of three of maximum uncertainty is considered. The chemical approaches air equilibrium when -Ln (f_g/f_w) range between 2.1 and -1.5. If -Ln (f_g/f_w) > 2.1 or -Ln (f_g/f_w) < -1.5, a net deposition or net volatilization of each PAH occurs at the station, respectively.

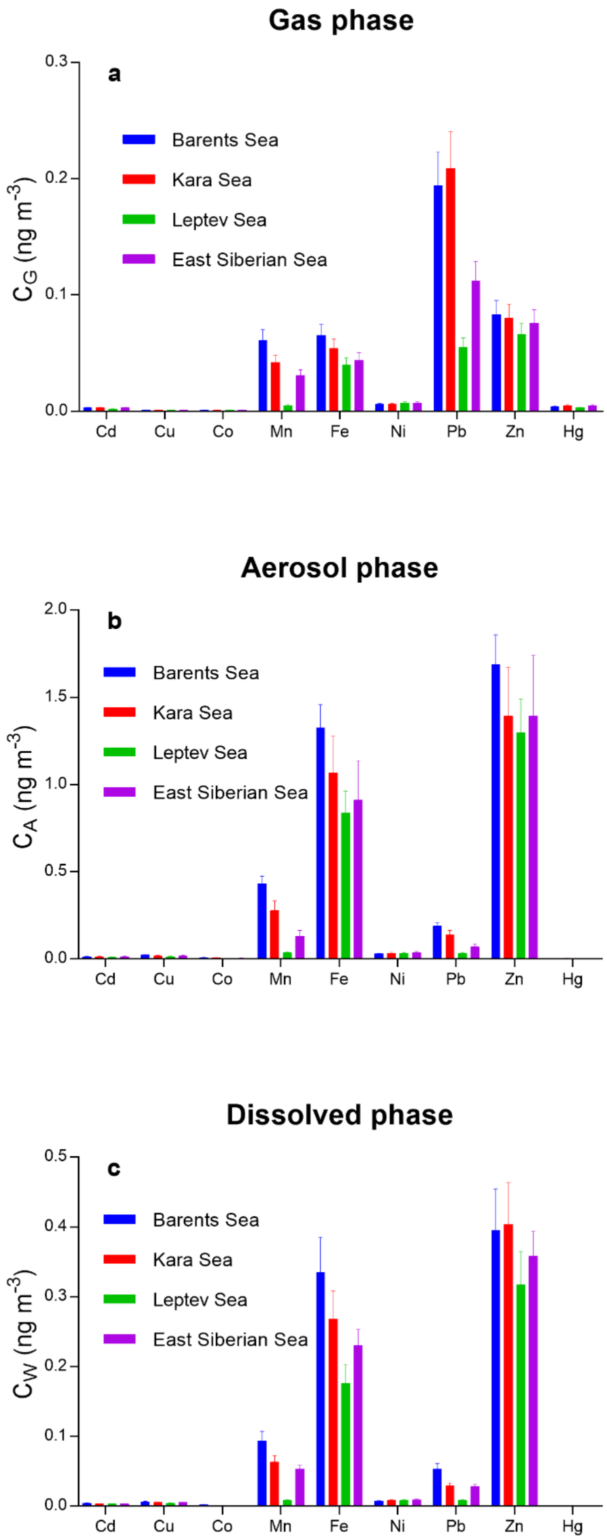


Figure S3. Pattern of heavy metals concentration in the oceanic atmosphere and water. Average and standard deviation of heavy metals concentrations for individual measured matrix; gas (a), aerosol (b) and dissolved phase (c). Bars represent the standard deviation of each heavy metal for each sea of Russian Arctic ocean.

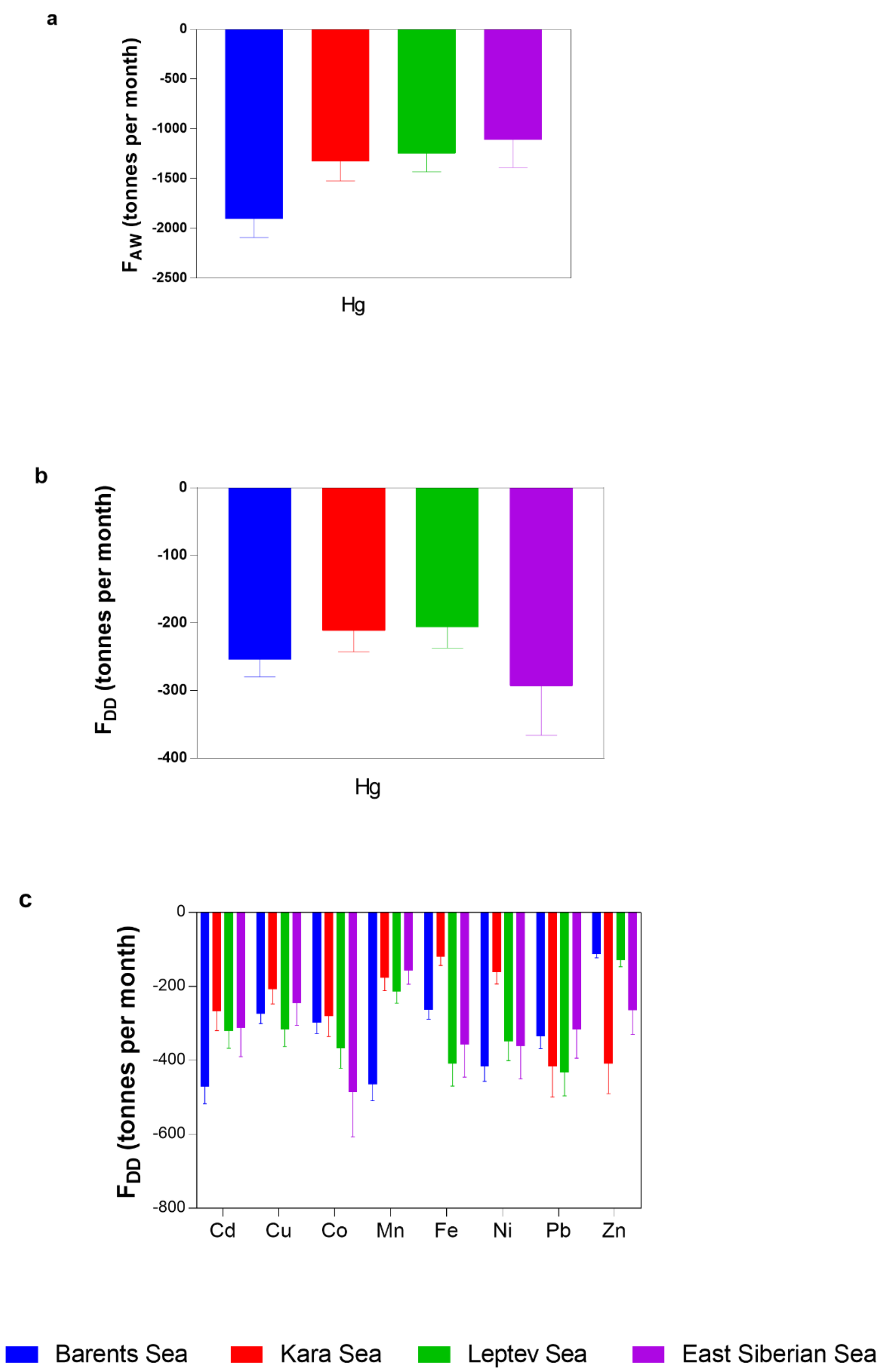


Figure S4. Estimates of oceanic atmosphere-ocean exchange of Hg. (a) Net diffusive air-water exchange of Hg (F_{AW}) and (b) dry deposition of Hg and other heavy metals (F_{DD}) fluxes averaged per month for the Barents, Kara, Laptev, and East Siberian Seas. Bars show standard deviation.

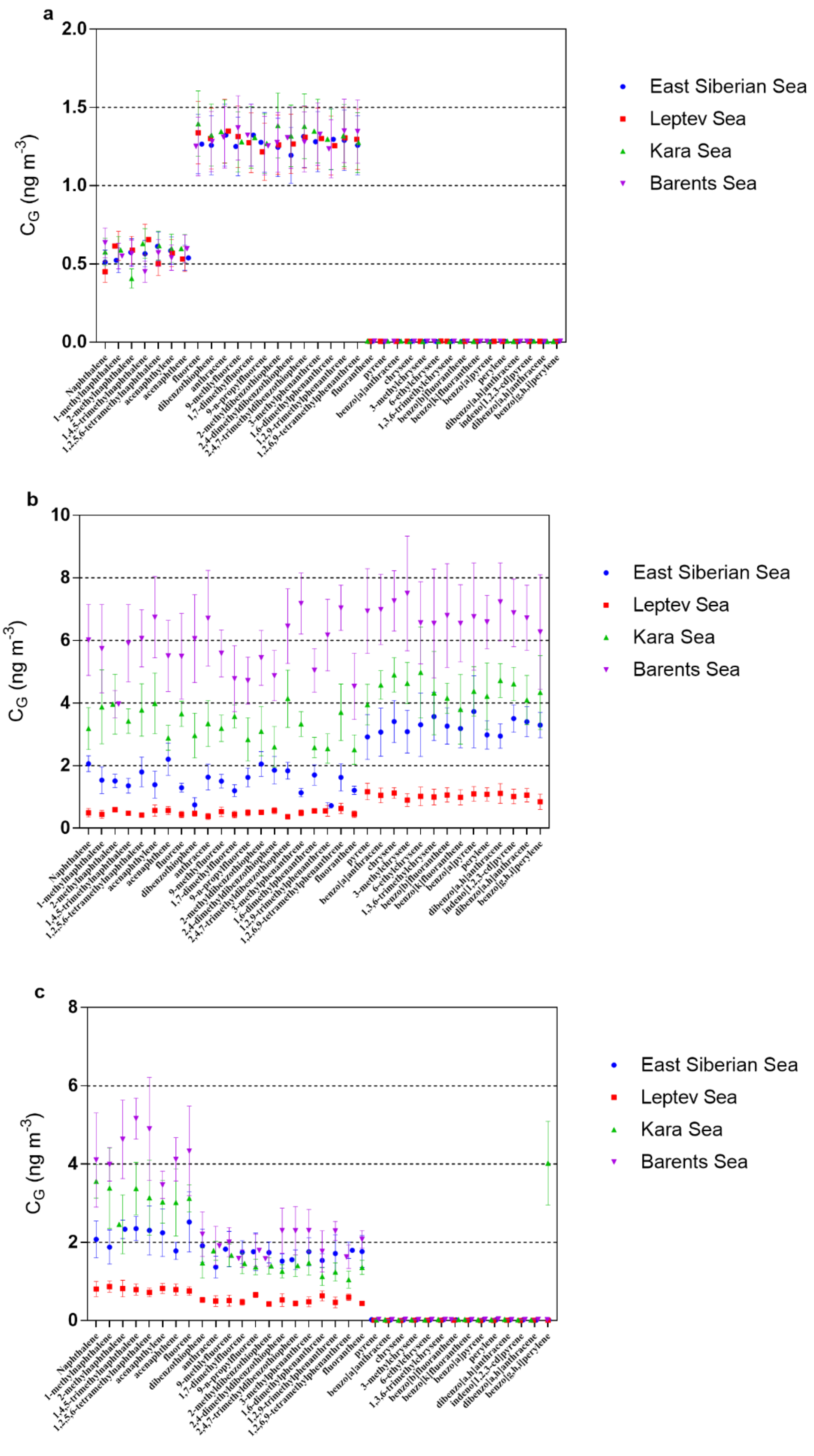


Figure S5. Concentration pattern of PAHs in the oceanic atmosphere and seawater. Mean and standard deviation of PAHs concentration for individual measured matrix; (a) gas, (b) aerosol, and (c) dissolved phase. Bars represent the standard deviation of individual PAH at each sea.

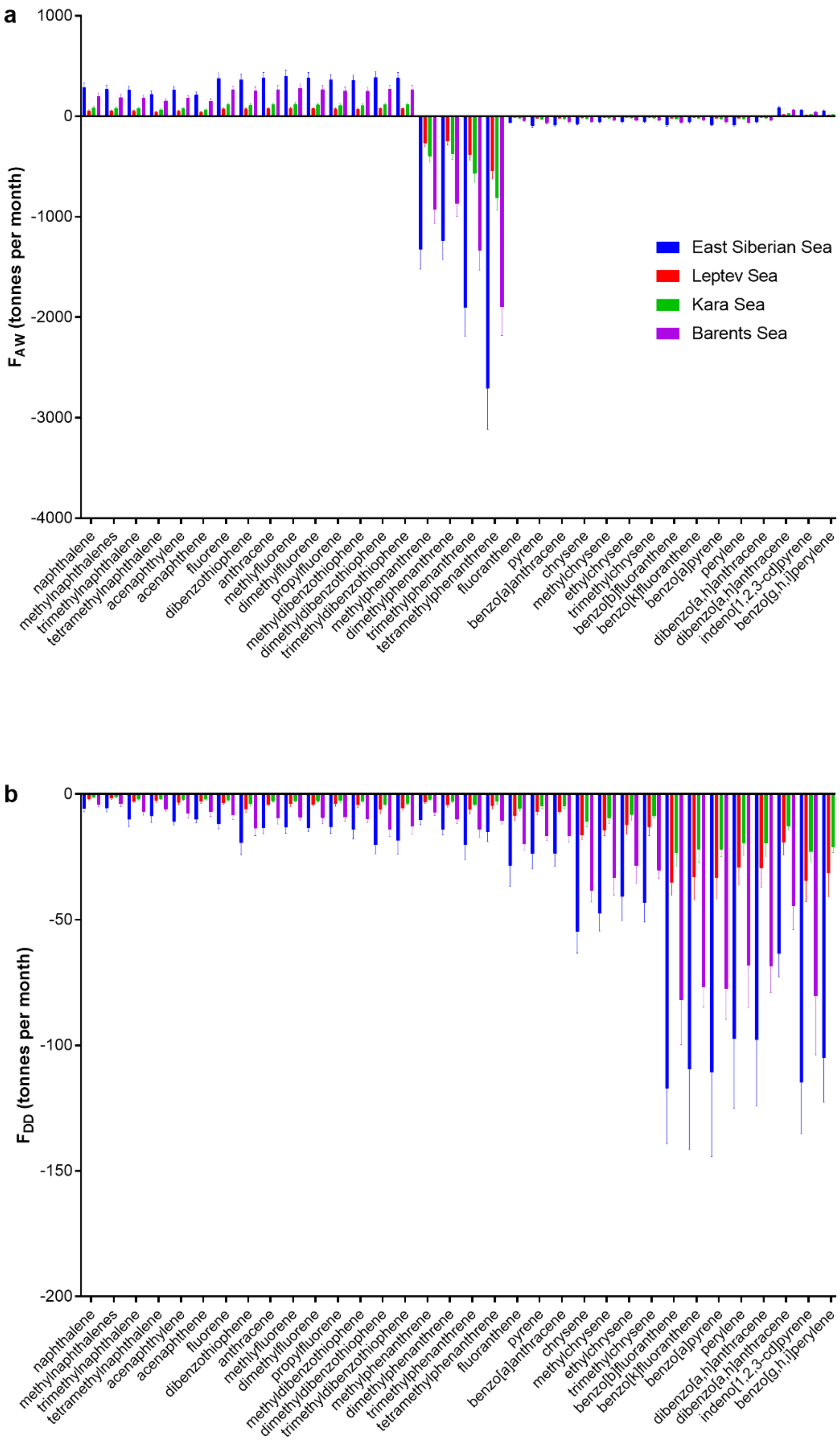


Figure S6. Estimated of atmosphere-ocean exchanges of PAHs in the Russian Arctic ocean. (a) Average net diffusive air-water exchange (F_{AW}) and (b) dry deposition (F_{DD}) fluxes per month for the East Siberian Sea, Barents Sea, Kara Sea and Leptev Sea. Bars represent standard deviation.

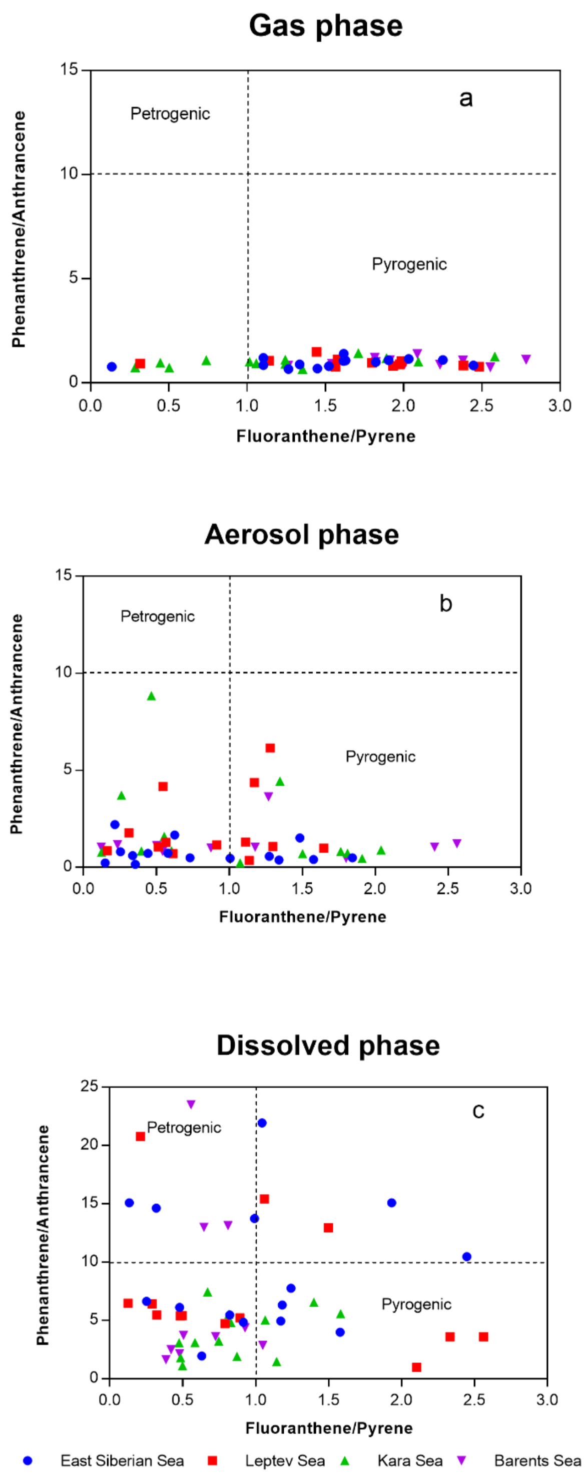


Figure S7. The diagnostic ratio of PAHs sources. The ratio of Phenanthrene/Anthracene to Fluoranthene/Pyrene for the gas (a), aerosol (b), and dissolved phases (c). the traditional attribution to pyrogenic and petrogenic PAHs (pairs of ratios) were used (Lima et al., 2005). The ratios were not used for characterization of biogenic PAHs due to the diagnostic ratios should be cautious to use for atmospheric samples (Katsoyiannis et al., 2011).

References

Katsoyiannis, A., Sweetman, A.J., Jones, K.C., 2011. PAH Molecular Diagnostic Ratios Applied to Atmospheric Sources: A Critical Evaluation Using Two Decades of Source Inventory and Air Concentration Data from the UK. Environmental Science & Technology 45, 8897-8906.
Lima, A.L.C., Farrington, J.W., Reddy, C.M., 2005. Combustion-Derived Polycyclic Aromatic Hydrocarbons in the Environment—A Review. Environmental Forensics 6, 109-131.