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2 **by Passive sampling**

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16 **Abstract**

17 The North Pacific-Arctic Oceans are important compartments for semi-volatile organic
18 compounds' (SVOCs) global marine inventory, but whether they act as a "source-sink" remains
19 controversial. To study the air-sea exchange and fate of SVOCs during their poleward long-
20 range transport, low-altitude atmosphere and surface seawater were measured for polycyclic
21 aromatic hydrocarbons (PAHs) by passive sampling from July to September in 2014. Gaseous
22 PAH concentrations ($0.67\text{-}13\text{ ng m}^{-3}$) were dominated by phenanthrene (Phe) and fluorene (Flu),
23 which displayed an inverse correlation with latitude, as well as a significant linear relationship
24 with partial pressure and inverse temperature. Concentrations of PAHs in seawater ($1.8\text{-}16\text{ ng}$
25 L^{-1}) showed regional characteristics, with higher levels near the East Asia and lower values in
26 the Bering Strait. The potential impact from the East Asian monsoon was suggested for gaseous
27 PAHs, which – similar to PAHs in surface seawater - were derived from combustion sources.
28 In addition, the data implied net volatilization of PAHs from seawater into the air along the
29 entire cruise; fluxes displayed a similar pattern to regional and monthly distribution of PAHs in
30 seawater. Our results further emphasized that air-sea exchange is an important process for PAHs
31 in the open marine environments.

32 **Keywords**

33 Polycyclic aromatic hydrocarbons; Low-density polyethylene; Air-sea exchange; Long-
34 range transport; High-latitude marine environment.

35 **1. Introduction**

36 Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the environments worldwide,
37 and some of them are toxic, carcinogenic and mutagenic (Bozlaker et al., 2008; Okona-Mensah
38 et al., 2005; Perera et al., 2005). Besides their petrogenic origin, PAHs are also generated during
39 the incomplete combustion of organic materials, like fossil fuels and biomass (Yunker et al.,
40 2002). As a class of semi-volatile organic compounds (SVOCs), they could arrive in the polar
41 area from temperate regions with subsequent deposition and re-volatilization, representing an
42 emerging concern in the Arctic like other conventional pollutants (Cai et al., 2016; Friedman
43 and Selin, 2012; Laender et al., 2011).

44 Atmospheric transport has been considered the primary pathway for PAHs transported
45 from the lower latitudes to the Arctic environments (Mulder et al., 2015; Dotel et al., 2020).
46 Previous studies showed that PAHs found in the Arctic seawater and sediments mainly
47 originated from natural underwater hydrocarbon seeps, while those in the air were from
48 atmospherically derived sources (Harvey et al., 2014; Yunker et al., 2011; Foster et al., 2015).
49 With the concern of climate change, the “polar sinks” for many conventional pollutants may
50 become secondary sources via air-water exchange, that is, the declining sea ice coverage and
51 rising temperature could lead to an accelerating release of PAHs from sea ice and seawater to
52 the atmosphere (Hung et al., 2010; Ma et al., 2011, 2013; Galban-Malagon et al., 2013). Thus,
53 studying PAHs in the atmosphere and related interfaces is helpful to better know the current
54 state of the PAH emission and their fates in the Arctic (Friedman et al., 2014).

55 Passive sampling is an effective monitoring technique for SVOCs, which is easy to operate,
56 cost-effective and with high enrichment of the target compounds, and has been applied in
57 various global monitoring projects (Lohmann et al., 2001; Harner et al., 2003; Meijer et al.,
58 2003; Jaward et al., 2004; Khairy and Lohmann, 2014; Mcdonough et al., 2014; Zhao et al.,
59 2018). This method integrates contaminant concentrations over time, representing time-
60 weighted averages (Stuer-Lauridsen, 2005; Shaw and Mueller, 2009; Wania and
61 Shunthirasingham, 2020). For PAHs, the freely-dissolved pollutants can be sampled with low-
62 density polyethylenes (LDPEs) (Khairy and Lohmann, 2014). Concentrations of target
63 compounds that do not reach equilibrium during the exposure period can be estimated relying

64 on the diffusive loss of performance reference compounds (PRCs) (Booij et al., 2002; Mayer et
65 al., 2003; Khairy and Lohmann, 2012).

66 Although previous studies have reported the distribution and direction of PAHs air-water
67 exchange in the northern Pacific and the Arctic, as well as fugacity model simulations, the
68 seasonal and regional trends of PAHs remain uncertain (Ke et al., 2017; Ma et al., 2013). Hence
69 the air-sea exchange process of PAHs from the North Pacific to the Arctic needs further research.
70 In this study, we performed spatially resolved air and water measurements during the sampling
71 cruise, and the objectives were to (1) obtain the spatial and temporal distribution characteristics
72 of atmospheric and dissolved PAHs in seawater from the North Pacific Ocean to the western
73 Arctic Ocean; (2) assess the source of gaseous and freely dissolved PAHs at most sites; (3)
74 derive the direction and magnitude of the air-sea flux exchange process of PAHs.

75 **2. Materials and methods**

76 **2.1 Area description**

77 During the Chinese sixth Arctic scientific expedition cruise from July to September in
78 2014, we collected 32 atmosphere and 16 surface seawater samples in the Japan Sea, Bering
79 Sea and Chukchi Sea onboard the R/V *Xuelong* (Snow Dragon). The Bering Strait, connecting
80 the Bering Sea with the Chukchi Sea, and linking the Asian and American continents, is the
81 boundary of the Arctic and Pacific Oceans. The Bering Sea is a semi-enclosed, high-latitude
82 sea that is almost divided equally between a deep basin (maximum depth 3500 m) and the
83 continental shelves (<200 m). The eastern broad (>500 km) shelf of the Bering Sea contrasts
84 with the narrow (<100 km) western shelf (Stabeno and Van Meurs, 1999). Water in the vast
85 (~500 km wide from east to west and ~800 km long from north to south) and shallow (~50 m)
86 Chukchi Sea (Arctic Ocean) is strongly forced by Pacific Ocean water entering through the
87 Bering Strait (Woodgate et al., 2005), which delivers heat, freshwater, nutrients, and carbon to
88 the Chukchi shelf and the Arctic Ocean.

89 In this study, there were 16 sampling stations (Table S1 in Supporting Information, SI), of
90 which PS-01 to PS-07 were located in the Sea of Japan and northwest Pacific Ocean, while PS-
91 08 to PS-10 in the Bering Sea and the Bering Straits, and PS-11 to PS-16 in the Arctic Ocean
92 (mainly in Chukchi Sea).

93 2.2 Materials Preparation and Field sampling

94 2.2.1 Preparation for LDPEs

95 Both atmospheric and seawater samplers were made of LDPEs with PRCs, which is
96 similar to the material used in semipermeable membrane devices; The inclusion of PRCs
97 provided a means to identify the absorption of hydrophobic PAHs by estimating dissipation
98 rates of PRCs (Booij et al., 2002; Lei et al., 2020). LDPEs (10 cm × 40 cm size, 50 μm thickness)
99 were cleaned in dichloromethane and n-hexane for 24 h respectively. Deuterated PAHs (pyrene-
100 d₁₀ and benzo [a] pyrene-d₁₂, namely Pyr-d₁₀ and BaP-d₁₂) were used as PRCs to infer the
101 equilibrium concentration of compounds in the passive samplers as in previous work (Booij et
102 al., 2002; McDonough et al., 2014). LDPEs were soaked in PRCs and continuously shaken for
103 one month to achieve homogenous uptake prior to deployments.

104 2.2.2 Simultaneous sampling in atmosphere and surface seawater

105 Atmospheric and surface-seawater LDPEs were deployed and collected simultaneously on
106 the underway R/V *Xuelong* in the Japan, Bering and Chukchi Seas (Fig. S1), and LDPEs were
107 changed every three days. The sampling site coordinates were calculated as the middle position
108 of the start and end of sampling positions.

109 Surface-seawater LDPEs were put into a stainless-steel pipe, and continuously exposed to
110 fresh marine surface seawater from the onboard seawater supply. We controlled the flow rate
111 of the seawater such that the LDPEs were submerged constantly. The atmospheric sampling
112 device was installed on the top deck, which was about 26 m above sea level. The device
113 consisted of two stainless-steel bowls, connected in the middle by a stainless-steel center shaft.
114 The LDPEs, thread on a metal wire, were fastened on the center shaft for sampling. All the
115 LDPE samples were sealed with an aluminum foil bag and stored at -20°C.

116 2.2.3 Other auxiliary parameters

117 Auxiliary parameters such as temperature and salinity were provided by the *Xuelong* ship
118 real-time monitoring system, and other parameters such as wind speed, wind direction and air
119 temperature were provided by the automatic weather station on board *Xuelong* ship.

120 2.3 Pretreatment and analysis

121 LDPE samples were thawed out at room temperature, then cleaned with Milli-Q water and

122 any excess water or biofouling was removed with KimWipes. 200 mL of n-hexane was added
123 to completely cover LDPEs after addition of 50 μ L 100 ppb PAHs recovery indicator surrogates
124 (acenaphthalene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂ and perylene-d₁₂, namely Acp-d₁₀, Phe-d₁₀,
125 Chry-d₁₂ and Pery-d₁₂ respectively). After extraction for 24 h, the n-hexane was decanted and
126 the extract was kept in a clean glass bottle. After a solvent exchange to dichloromethane, and
127 repeating the above steps, extracts were combined. The extract was concentrated to 1mL in a
128 30°C water bath by a fully automatic sample concentrator, transferred to a volumetric tube and
129 slowly purged to 100 μ L with high-purity nitrogen. Then 50 ng of deuterated terphenyl and 35
130 ng of 2, 4, 6-Tribromobiphenyl were added as internal standards. The extract was sealed and
131 frozen for storage before analysis. The weight of the extracted LDPE samples was recorded
132 before and after treatment.

133 An Agilent 6890-5973 GC-MS equipped with a DB5-MS quartz capillary column (30 m
134 \times 0.25 mm i.d. \times 0.25 μ m, J&W Scientific Inc., Folsom, U.S.A.) was used to detect PAHs. The
135 high purity helium was used as carrier gas with the flow rate of 1mL min⁻¹. The temperature
136 programming of chromatography column started at 90 °C with three 3 minutes hold, then
137 reached 110 °C at 5 °C min⁻¹(holding 2 minutes), increased by 8 °C min⁻¹ until 200 °C (holding
138 3 minutes), and finally reached 315 °C at 5 °C min⁻¹ five, keeping the final temperature for 5
139 minutes.

140 **2.4 Quality assurance and quality control**

141 Avoiding contamination was an important consideration in all steps associated with the
142 extraction and analysis of LDPEs. All glassware used during pretreatment were cleaned, baked
143 at 450°C for at least 4 hours, and thoroughly solvent-rinsed before use. The field blanks were
144 regularly included in the sampling protocol, and included when samplers were changed during
145 deployment and retrieval. Method detection limits (MDLs) were calculated as three times the
146 standard deviation of the average field blank concentration. The MDL of the target compounds
147 are listed in SI as well as instrument detection limits. All of the data were blank-corrected.
148 When the concentration of the target compounds was less than the detection of limits, half of
149 MDL was taken as its concentration value (Antweiler and Taylor, 2008).

150 22 PAHs were detected in this study. In addition to the 16 priority PAHs listed by U.S.

151 EPA, the other six compounds were Biphenyl (Biph), 1-Methylphenanthrene (1-MePhe), Retene
152 (Ret), Benzo[e]pyrene (BeP), Perylene (Pery) and Benzo[j]fluoranthene (BjF) (Table S2 in SI).
153 Due to the high environmental background concentration of naphthalene, it will not be
154 discussed in this study. In order to improve the quality and credibility of the data, if the
155 concentration of a certain target compound was greater than MDL but detected at less than 20%
156 of the total sites, it was omitted from the discussion. A total of nine PAHs in atmospheric
157 samples were regularly detected, which included phenanthrene (Phe), fluorene (Flu), Phe,
158 anthracene (Ant), 1-MePhe, fluoranthene (FluA), pyrene (Pyr), chrysene (Chry),
159 benzo[b]fluoranthene (BbF)/ benzo[k]fluoranthene (BkF) (because the peaks of BbF and BkF
160 were hard to chromatographically separate, the total concentration of BbF/BkF are reported).
161 While 11 PAHs in surface seawater samples were effectively detected, which included Flu, Phe,
162 Ant, 1-MePhe, FluA, Pyr, Chry, Biph, benz[a]anthracene (BaA), BbF/BkF. Concentrations of
163 PAHs in the samples were blank-corrected for the amounts detected in the field blanks, but not
164 recovery corrected. The average recovery rates of the four surrogates that Acp-d₁₀, Phe-d₁₀,
165 Chry-d₁₂, and Pery-d₁₂ were 70 ± 12, 75 ± 15, 85 ± 13, and 74 ± 18% respectively.

166 For the uncertainty analysis, it is difficult to estimate the overall uncertainty of air-water
167 exchange by passive sampling, because it involves multiple mathematical functions and values
168 that have both normal and lognormal errors associated with them. Additionally, the
169 uncertainties in H⁰ are not well characterized, causing the uncertainty associated with the
170 temperature- and salinity corrections were not included.

171 2.5 Calculations and data analysis

172 2.5.1 Calculations of PAH concentrations

173 For each compound, the fraction of equilibrium (f) achieved for each compound was
174 determined by fitting the equilibrium of the PRCs using temperature-corrected air-water
175 partitioning coefficient in LDPEs (K_{PE}) values to a model curve derived from equation (1) (Liu
176 et al., 2016),

$$177 \quad f = 1 - e^{-\frac{R_s t}{K_{PE} M_{PE}}} \quad (1)$$

178 Where R_s (L day⁻¹) is the sampling rate defined as the volume of water or air that comes
179 into contact with the sampler per day; t is deployment time (days); M_{PE} is the PE weight (kg);

180 the values of R_s can be estimated using nonlinear least squares methods, by considering f as a
 181 continuous function of K_{PE} , with R_s as an adjustable parameter using Excel Solver to obtain the
 182 best fit (Booij and Smedes, 2010). The average gaseous sampling rate of PAHs was $1\,700 \pm 1$
 183 $500\text{ m}^3\text{ day}^{-1}$, among which the Pacific Ocean and the Bering Sea was $620 \pm 410\text{ m}^3\text{ day}^{-1}$,
 184 however the Arctic Ocean was $3\,100 \pm 1\,300\text{ m}^3\text{ day}^{-1}$, resulted from different wind speed and
 185 directions described below. The aqueous sampling rate of PAHs was $140 \pm 54\text{ L day}^{-1}$.

186 Gaseous and freely dissolved concentrations, $C_{A/W}$ of compounds were calculated from
 187 the equation (2),

188
$$C_{A/W} = \frac{C_{PE} - C_{Blank}}{K_{PE} \left(1 - e^{-\frac{R_s t}{K_{PE} M_{PE}}} \right)} \quad (2)$$

189 Where C_{PE} is the PE-normalized concentrations. For more details, see the Supporting
 190 Information.

191 **2.5.2 Brief description of calculation and two-film model**

192 The Whitman two-film resistance model was used for the air-sea exchange flux (F_{aw})
 193 calculation in the modified version (Liss and Slater, 1974).

194
$$F_{a/w} = v_{a/w} \left(C_w - \frac{C_a}{K_{aw}} \right) \quad (3)$$

195 where $F_{a/w}$ is calculated with the mass transfer velocity ($v_{a/w}$), the concentrations in seawater
 196 and atmosphere, C_w and C_a , and air-water partitioning coefficient corrected by ambient
 197 temperature, K_{aw} (Liu et al., 2016). Calculation details of PAHs air-sea exchange fluxes at
 198 different sites are listed in SI from Table S6 to S12.

199 **2.6 Air mass back trajectories**

200 The NOAA's HYSPLIT model was used to track the origins of air masses (Draxler and
 201 Hess, 1998). Air mass back trajectories were set as 12 h steps that traced back the air masses
 202 for 5 days, using the sampling height as arrival height.

203

204 **3. Results and discussion**

205 **3.1 PAHs in the atmosphere**

206 **3.1.1 Concentrations and distributions**

207 Total gaseous concentrations of Σ_9 PAH ranged from 0.67 to 13 ng m⁻³ with the mean value
208 of 3.7 ± 3.0 ng m⁻³, close to previous data of 0.93-93 ng m⁻³ for Σ_{15} PAH reported over the North
209 Pacific and Arctic Ocean in 2003, as well as 0.91-7.4 ng m⁻³ with a mean of 3.3 ± 1.7 ng m⁻³
210 for Σ_{18} PAH reported in 2010 (Ding et al., 2007, Ma et al., 2013). Observation showed the
211 maximum concentrations occurred at PS-01 located in the Bohai Sea, and lowest at PS-16 in
212 the Arctic Ocean (Fig. 1, Table S3).

213 In this study, nine different PAHs were regularly detected in most gaseous samples,
214 including three-ring PAHs like Flu, Phe, 1-MePhe, Ant, and four-ring PAHs like FluA, Pyr, and
215 Chry. Higher molecular weight PAH concentrations in the atmosphere were typically below
216 their limits of detection. Across the entire sampling cruise, Phe displayed the highest average
217 contribution of 52% to Σ_9 PAH, followed by Flu, which contributed another 44%. Hence, the
218 cumulative contributions of other congeners were less than 5 %. Our results mirror previous
219 results, in that Phe was also the dominant compound among the gas phase PAHs, contributing
220 50% to Σ_{15} PAH over the North Pacific and Arctic Ocean (Ding et al., 2007).

221 **3.1.2 Decreasing distribution with latitude**

222 Overall, a significant negative correlation was observed between gaseous Σ_9 PAH and
223 latitude (the coefficients of determination, R^2 was 0.61, the P-value < 0.0010). The partial
224 pressure of seven PAH congeners were calculated by a modified Clausius-Clapeyron equation
225 (Venier et al., 2012), these results were obviously consistent with the trends in concentration
226 with temperature. The mobility of PAHs was usually reduced by decreasing temperature, which
227 contributed to decreasing volatility of PAHs, especially for higher molecular weight PAHs. As
228 shown in Fig. 2, the partial pressure of FluA, Pyr and Chry decreased faster than for the low
229 molecular weight PAHs such as Flu and Phe (All the R^2 and P-values are given in SI). Higher
230 molecular weight PAH congeners were more sensitive to temperature change, in line with
231 expectations for gaseous PAH concentrations with latitude (Fig. 2).

232 On the other hand, PAHs are more susceptible to photochemical-degradation in the

233 atmosphere. The concentration ratios of Flu to Phe were positively related to latitude ($R^2=0.58$,
234 $P<0.0010$) from the North Pacific to the Arctic (Figure 1); and the ratio FluA/(FluA+Pyr) was
235 greater than 0.5 at all stations (Fig. 4). The total photochemical residence time (τ_{total}) of Flu and
236 FluA were derived as 21 and 20 hours, and 9 and 5 hours for Phe and Pyr, respectively (Keyte
237 et al., 2014); the observed low concentrations of Ant in the atmosphere were likely caused by
238 its 2hours of τ_{total} . Furthermore, the atmospheric half-life of Flu is higher than Phe, which
239 means higher removal rates occurred in Phe, and Flu presents a greater transmission potential
240 than Phe for long-range atmospheric transport (LRAT) (Halsall et al., 2001).

241 3.1.3 Influence of air mass

242 Diagnostic ratios of gaseous PAHs were calculated, but need to be interpreted with caution,
243 because the ratios might be affected by potential post emission processes. 1-MePhe/Phe in the
244 atmosphere were less than 0.50, implying that the source of the PAHs could be attributed to
245 combustion processes (Yunker et al., 2002; Deka et al, 2016; Wu et al., 2019). This was further
246 supported by the isomeric ratios of FluA/(FluA+Pyr) that ranged from 0.42-0.82; a ratio greater
247 than 0.5 indicates the main sources of grass, wood or coal combustions, and between 0.4 to 0.5
248 usually suggests petrogenic combustion (Qu et al., 2019; Qi et al., 2020).

249 At the mid-latitude sites, the air mass mainly originated from the coast of China, Korea,
250 Japan and Russia, and close-by terrestrial regions as indicated by the air mass back trajectories
251 (Fig. S7 and S8 in SI). With the trajectories of air mass that was used to study the origin of
252 atmospheric PAHs in Japan and other neighboring areas, high concentrations of PAHs and
253 emissions have been already observed in East Asian areas (Ohura et al., 2004; Primbs et al.,
254 2007). Continuously decreasing concentrations of PAHs occurred from the Bering Sea to the
255 Arctic, but increased again between PS-09 and PS-11, where back trajectories indicated the air
256 had passed through Alaska and Siberia, especially on Kamchatka peninsula, consistent with the
257 impact of terrestrial source (Fig. S8 in SI). According to the air mass back trajectories, the
258 source of the atmosphere PAHs in July was significantly affected by the southwest monsoon,
259 which is also an important pathway for long-range transport.

260 3.2 PAHs in the seawater

261 3.2.1 PAH profiles in seawater

262 The concentrations of total freely dissolved \sum_{11} PAH in the surface seawater ranged from
263 1.8 to 16 ng L⁻¹ with the mean value of 7.7 ± 4.6 ng L⁻¹. The maximum concentrations occurred
264 at PS-03 on the northeast coast of Japan, followed by station PS-02 and PS-04, and the
265 minimum was observed at PS-10 in the Bering Strait (Fig. 3, Table S4). A total of 11 different
266 PAHs were regularly detected in the freely-dissolved phase in the seawater samples, including
267 Biph, Flu, Phe, 1-MePhe, Ant, FluA, Pyr, and Chry, BaA, BbF/BkF. The concentrations of
268 higher molecular weight PAHs in seawater were typically below the limits of detection, similar
269 to the atmosphere.

270 The ratios of 1-MePhe/Phe and FluA/(FluA+Pyr) indicated the main sources of
271 combustions included many types (Yunker et al., 2002; Qu et al., 2019; Qi et al., 2020). The
272 results in seawater were consistent to previous studies in the North Pacific and Arctic Ocean
273 (Ding et al., 2007; Ma et al., 2013).

274 While Phe also dominated the dissolved \sum_{11} PAH, its average contribution was only 36%.
275 Hence more PAHs were regularly present beyond Phe, including Flu, which contributed 25%,
276 FluA (11%), Pyr (10%), in addition 1-MePhe and Biph were 8 % and 5 %, respectively. Other
277 congeners like Ant, BaA, BbF/BkF were only detected in a few of the samples beyond the
278 Bering Sea (for details see SI), whose contributions were less than 4 %. The combined
279 influences of sources like rivers, runoff, currents as well as biogeochemical process cause more
280 higher molecular weight PAHs to be present in the surface seawater (Sambrotto, 1984;
281 McDonough et al., 2014). We speculate that differences in biodegradation and photochemical-
282 degradation of PAHs increased the proportion of higher molecular weight PAHs in seawater
283 (González-Gaya et al., 2019). Bacterial degradation rate constants (K_D) showed a significant
284 inverse correlation with K_{ow} , which means the capacity to biodegrade higher molecular weight
285 and hydrophobic PAHs (i.e., FluA, Pyr, Chry, BbF/BkF) were slower than for lighter weight
286 PAHs (Table S5) (Tucca et al., 2020). Besides, higher molecular weight PAHs in the air sorb to
287 aerosol according their higher octanol-air ratios, contributing to wet and dry deposition entering
288 seawater.

289 3.2.2 Changes of freely-dissolved PAH distribution with region

290 Freely dissolved Σ_{11} PAH concentrations varied with sampling locations as well, but
291 displayed obvious regional trends instead of correlation with latitude. They ranged from 12 to
292 16 ng L⁻¹ in the Japan Sea to the North Pacific Ocean, located in a mid-latitude temperate zone.
293 Concentration were lower in the nearby Bering Strait ranging only from 1.8 to 4.8 ng L⁻¹, as
294 well as sites in the Arctic Ocean (2.7-6.5 ng L⁻¹). In general, dissolved Σ_{11} PAH concentrations
295 closer to shore were relatively higher than those in the open ocean (Fig. 3).

296 Lower concentrations of seawater Σ_{11} PAH were present at station PS-08, PS-09 and PS-
297 10 in the Bering Strait, which was known as one of the most productive waters in the Arctic
298 Ocean. Likely removal of PAHs by high amounts of biogenic particles significantly decreased
299 the concentration of PAHs in the ocean, where the plankton biomass was higher, consistent with
300 the relevance of the biological pump (González-Gaya et al., 2019). Another reason for low
301 concentrations of Σ_{11} PAH in the Arctic Ocean are the oceans' long residence time, as well as
302 the weak sea ice melting in summer. The ocean current exchange is relatively slow, causing the
303 residence time of surface water to be about 10 years. Melting sea ice has been recognized as an
304 important factor controlling the distribution of PAHs in the Arctic, where only part of the sea
305 ice melts even in summer (MacDonald et al., 2000). The lower salinity supported that
306 continental runoff or melting ice rather than ocean currents were the pathways of PAHs into the
307 surface water, and the atmospheric deposition was also a key source (see below).

308 3.3 Air-sea exchange of PAHs with two-film model

309 3.3.1 General net volatilization

310 The air-sea exchange fluxes of the seven PAHs was generally dominated by net
311 volatilization especially from the North Pacific to the Arctic (Fig. 5, Table S12). Generally,
312 fluxes of the more volatile PAHs especially for Flu and Phe were greater and nearly accounted
313 for >70% of all (Table S12 in SI), based on their dominant contribution to gaseous and free-
314 dissolved PAHs. The maximum values of volatilization and deposition fluxes of Σ_9 PAHs were
315 observed at site PS-04 (11 $\mu\text{g m}^{-2} \text{day}^{-1}$) and PS-01 (-2.5 $\mu\text{g m}^{-2} \text{day}^{-1}$) respectively. Flux
316 distributions indicated that the deposition was only observed near land from Shanghai to the
317 Bohai Sea, while net volatilizations were more widespread. For instance, Flu dominated the

318 flux at site PS-04 with the value of $4.2 \mu\text{g m}^{-2} \text{ day}^{-1}$, and Phe at site PS-01 was $-5.2 \mu\text{g m}^{-2} \text{ day}^{-1}$,
319 ¹, due to the greatest concentrations of dissolved Flu at PS-04 and gaseous Phe at PS-01
320 respectively. The effect of volatilization from coastal waters with high PAH levels has reported
321 in other PAH-impacted regions such as the Atlantic, Narragansett Bay (USA) and the southeast
322 Mediterranean (Nizzetto et al., 2008; Castro-Jiménez et al., 2012; Lohmann et al., 2011). The
323 fluxes were mainly contributed by three-ring PAHs, while the fluxes of four-ring PAHs showed
324 less variation in the North Pacific and the Arctic.

325 **3.3.2 Flux trend closely coupling with dissolved phase**

326 The derived air-water exchange fluxes correlated significantly to regional and monthly
327 changes, similar to the freely-dissolved PAH distributions, which might imply the one of driver
328 by concentration gradients between seawater and air (Fig. 5). Volatilizations dominated in the
329 air-sea exchange because the seawater concentrations corrected by K_{aw} were one to three orders
330 of magnitudes higher than equivalent concentrations in the atmosphere.

331 As for individual congeners, there were no clear trends for three-ring PAHs, but diverse
332 ones for higher-ring PAHs, especially FluA and Pyr declined with increasing latitude (Fig. S5
333 in SI). These results verified that higher molecular weight PAHs were more sensitive to changes
334 with temperature. PAHs are moderately volatile and hydrophobic, which facilitates their
335 partitioning from air and water into organic phases (Nizzetto et al., 2010). Obvious outputs of
336 biogenic particles occurred in the Bering Strait and caused a significant decrease in seawater
337 concentration as well as fluxes. In the Arctic, low PAHs fluxes were driven basically by low
338 atmospheric and seawater concentrations. However, the net volatilizations only had a minor
339 impact on atmospheric concentration. According to the long-range transport and diffusion
340 advection of PAHs, the atmospheric concentrations tend to decrease as the latitude increases,
341 so the transports depend largely on temperature changes. In our study, strong correlations were
342 observed for air-sea exchange fluxes with concentrations rather than temperature.

343 **3.4 Implication for the source-sink pattern of PAHs**

344 **3.4.1 Source pattern of PAHs from the Pacific to the Arctic**

345 For further analysis, principal component analysis (PCA) was used to elucidate linear
346 combinations of PAHs, to distinguish between the samples to assess different sources (Nemr et

347 al., 2005). Two compounds were obtained from PCA, namely the first principal component
348 (PC1) and second principal component (PC2), contributed 74% to the total variance (Fig. 4).
349 Correlation analysis showed high relevance of PC1 for four-ring PAHs, such as FluA and Pyr
350 ($r=0.98$), FluA and Chry ($r=0.90$), Pyr and Chry ($r=0.94$); and PC2 represented mainly three-
351 ring PAHs such as Flu and Phe ($r=0.82$), Flu and Ant ($r=0.56$), Phe and 1-MPhe ($r=0.67$). The
352 scores on PCA showed that all the sites in the Bering Sea and Arctic were concentrated together
353 in the negative axis of PC1 and PC2, while sites in the North Pacific were more dispersed.

354 The diagnostic ratios and PCA analysis provided qualitative information about the spatial
355 patterns of PAH sources. Based on the analysis mentioned earlier, we inferred that sources of
356 seawater and atmospheric PAHs in the Bering Sea and Arctic were mainly from combustion
357 processes. In the Arctic, the diagnostic ratios of PAH concentrations in seawater were similar
358 to that in atmosphere, which might provide the evidence that PAHs reached high latitudes by
359 long-range atmosphere transport (LRAT). Hence the atmospheric concentrations contributed
360 only low levels in the high latitudes, and combined with sea ice melting, runoff and other
361 biogeochemical process to affect the ratio characteristics. On the other hand, both of the
362 seawater and atmospheric PAHs in the Pacific Ocean were also mainly derived from
363 combustion processes. The difference is that the North Pacific is known as an important cruise
364 routes area, which potentially contributes additional sources factors, complicating the seawater
365 PAHs. Therefore, petroleum combustion emitted by ships is an inevitable source for PAHs in
366 addition to runoff, ocean currents and atmospheric deposition.

367 **3.4.2 Net volatilization prospect under climate changing**

368 Our results illustrated that the majority of PAHs displayed a net volatilization trend from
369 East Asia to the Arctic, which was on the contrary of the previous studies (Zhong et al., 2012;
370 Ma et al., 2013). The significant differences in the fluxes were partly attributed to the different
371 concentrations of gaseous and dissolved PAHs between these two studies whose samples were
372 from different years. The time lag to previous studies might have been sufficient to cause an
373 increase in PAH concentration in surface seawater for the ongoing-emitted PAHs year by year.
374 In addition, East Asia is a possible continental source area and has been estimated to contribute
375 greatly to the global emission inventory of PAHs (Shen et al., 2013). Furthermore, sea surface
376 temperatures (SSTs) in August 2014 were as much as 4 °C warmer than the 1982-2010 August

377 mean in the Bering Strait and the sixth smallest Arctic sea ice extent by the satellite record
378 (1979-2014) occurred in the summer of 2014 (Chen et al., 2016), which might partially explain
379 the different results reported here. Lastly, sampling of PAHs by passive sampling only captures
380 freely dissolved or gas-phase compounds, which should lead to air-water exchange fluxes not
381 impacted by inadvertent capture of PAH bound to colloids or small particles.

382 Some persistent organic pollutants, whose primary emissions have been reduced, are
383 suggested having iterative processes (including deposition, volatilization and re-deposition) in
384 the changing Arctic (Cai et al., 2012). Since the ice will prevent the escape of PAHs in winter,
385 we can assume that atmospheric PAHs will deposit in snow and ice by dry/wet deposition
386 processes and the Arctic turned into a sink again. In other words, as a result of global warming
387 with sea ice retreat, whether the polar region is a sink or secondary source depends on the
388 seasonal variety. The air-sea exchange fluxes in our study displayed significantly lower in
389 September than in July (Fig. 5), which might be driven by decreasing temperature and
390 weakened monsoon. PAH concentrations and fluxes are thus likely affected by temporal
391 changes, but more evidence is needed (Fig. S6 in SI). Combining this with our result that fluxes
392 were consistent with surface seawater PAHs concentrations, then seawater might dominate the
393 air-sea exchange when not covered by sea ice. But whether the hypothesis is reasonable or not
394 need to be further studied, and which might determine the role of the Arctic as “sink” or “source”
395 of PAHs.

396 **4 Conclusions**

397 This study focused on the air-sea exchange process of PAHs, relying on LDPEs passive
398 sampling from the North Pacific to Arctic. The gaseous concentrations of \sum_9 PAH ranged from
399 0.67 to 13 ng m⁻³ and displayed a significant decreasing trend with latitude, which was
400 dominated by long-range transport and photochemical-degradation of PAHs. Different
401 distributions were explained by the air mass back trajectories, coupled with the influence of air-
402 sea exchange and dry/wet deposition processes. The concentrations of total freely dissolved
403 \sum_{11} PAH ranged from 1.8 to 16 ng L⁻¹ whereas higher molecular weight PAHs showed more
404 presence. The changes in PAH profiles can likely be attributed to their relative capacity to
405 undergo biodegradation and dry/wet deposition. In addition, regional distributions were shown

406 in freely dissolved PAHs, showing high levels in the North Pacific. The lower levels were
407 impacted by biogenic particle removals in the Bering Sea, and were attributed to slow renewal
408 of seawater and melting ice in the Arctic. Molecular ratios of the PAHs in atmosphere and
409 surface seawater indicated combustion sources, and the source indication might provide some
410 evidence for LRAT of high-latitude marine environmental PAHs. Overall, the air-sea fluxes of
411 PAHs presented mostly net volatilizations with special regional and monthly changes,
412 controlled by seawater concentrations. The air-sea exchange process showed only a relatively
413 minor importance of air concentrations, instead the fluxes and dry/wet depositions from
414 atmosphere to seawater might be more important especially in the Arctic.

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420 **Reference**

- 421 Antweiler, R. C., Taylor, H. E., 2008. Evaluation of statistical treatments of left-censored environmental
422 data using coincident uncensored data sets: I. Summary statistics. *Environmental Science &*
423 *Technology*, 42(10): 3 732-3 738.
- 424 Booij, K., Smedes, F., 2010. An improved method for estimating in situ sampling rates of nonpolar
425 passive samplers. *Environmental Science & Technology*, 44(17): 6 789-6 794.
- 426 Booij, K., Smedes, F., van Weerlee, E. M., 2002. Spiking of performance reference compounds in low
427 density polyethylene and silicone passive water samplers. *Chemosphere*, 46(8): 1 157-1 161.
- 428 Bozlaker, A., Muezzinoglu, A., Odabasi, M., 2008. Atmospheric concentrations, dry deposition and air-
429 soil exchange of polycyclic aromatic hydrocarbons (PAHs) in an industrial region in Turkey.
430 *Journal of Hazardous Materials*, 153(3): 1 093-1 102.
- 431 Cai, M. G., Liu, M. Y., Hong, Q. Q., Lin, J., Huang, P., Hong, J. J., Wang, J., Zhao, W. L., Chen, M., Cai,
432 M. H., Ye, J., 2016. Fate of polycyclic aromatic hydrocarbons in seawater from the Western
433 Pacific to the Southern Ocean (17.5 degrees °N to 69.2 degrees °S) and their inventories on the
434 Antarctic Shelf. *Environmental Science & Technology*, 50(17): 9 161-9 168.
- 435 Cai, M. H., Ma, Y. X., Xie, Z. Y., Zhong, G. C., Moeller, A., Yang, H. Z., Sturm, R., He, J. F., Ebinghaus,
436 R., Meng X. Z., 2012. Distribution and air-sea exchange of organochlorine pesticides in the
437 North Pacific and the Arctic. *Journal of Geophysical Research-Atmospheres*, 117: D06311.
- 438 Castro-Jiménez, J., Eisenreich, S. J., Mariani, G., Skejo, H., Umlauf G., 2012. Monitoring atmospheric
439 levels and deposition of dioxin-like pollutants in sub-alpine Northern Italy. *Atmospheric*
440 *Environment*, 56: 194-202.
- 441 Chen, H. W., Alley, R. B., Zhang, F., 2016. Interannual Arctic sea ice variability and associated winter
442 weather patterns: A regional perspective for 1979-2014. *Journal of Geophysical Research-*
443 *Atmospheres*, 121(24): 14 433-14 455.
- 444 Deka, J., Sarma, K. P., Hoque, R. R., 2016. Source contributions of Polycyclic Aromatic Hydrocarbons
445 in soils around oilfield in the Brahmaputra Valley. *Ecotoxicology and Environmental Safety*,
446 133: 281-289.
- 447 Ding, X., Wang, X. M., Zhou, Q. X., Cai, H. X., Bi, X. M., Li, G. S., Zheng, M., Guo, Y. S., Jia, M. F.,
448 Poeschl, U., 2007. Atmospheric polycyclic aromatic hydrocarbons observed over the North
449 Pacific Ocean and the Arctic area: Spatial distribution and source identification. *Atmospheric*
450 *Environment*, 41(10): 2 061-2 072.
- 451 Dotel, J., Gong, P., Wang, X. P., Pokhrel, B., Wang, C. F., Nawab, J., 2020. Determination of dry
452 deposition velocity of polycyclic aromatic hydrocarbons under the sub-tropical climate and its
453 implication for regional cycling. *Environmental Pollution*, 261: 114143.
- 454 Draxier, R. R., Hess, G. D., 1998. An overview of the HYSPLIT_4 modelling system for trajectories,
455 dispersion and deposition. *Australian Meteorological Magazine*, 47(4): 295-308.
- 456 Foster, K. L., Stern, G. A., Carrie, J., Bailey, J. N. L., Outridge, P. M., Sanei, H., Macdonald, R. W., 2015.

457 Spatial, temporal, and source variations of hydrocarbons in marine sediments from Baffin Bay,
458 Eastern Canadian Arctic. *Science of The Total Environment*, 506: 430-443.

459 Friedman, C. L., Selin, N. E., 2012. Long-range atmospheric transport of polycyclic aromatic
460 hydrocarbons: a global 3-D model analysis including evaluation of Arctic sources.
461 *Environmental Science & Technology*, 46(17): 9 501-9 510.

462 Friedman, C. L., Zhang, Y. X., Selin, N. E., 2014. Climate Change and Emissions Impacts on
463 Atmospheric PAH Transport to the Arctic. *Environmental Science & Technology*, 48(1): 429-
464 437.

465 Galban-Malagon, C. J., Del Vento, S., Berrojalbiz, N., Ojeda, M. J., Dachs, J., 2013. Polychlorinated
466 biphenyls, hexachlorocyclohexanes and hexachlorobenzene in seawater and phytoplankton
467 from the Southern Ocean (Weddell, South Scotia, and Bellingshausen Seas). *Environmental
468 Science & Technology*, 47(11): 5 578-5 587.

469 González-Gaya, B., Martínez-Varela, A., Vila-Costa, M., Casal, P., Cerro-Galvez, E., Berrojalbiz, N.,
470 Lundin, D., Vidal, M., Mompean, C., Bode, A., Jimenez, B., Dachs, J., 2019. Biodegradation as
471 an important sink of aromatic hydrocarbons in the oceans. *Nature Geoscience*, 12: 119-125.

472 Halsall, C. J., Sweetman, A. J., Barrie, L. A., Jones, K. C., 2001. Modelling the behaviour of PAHs during
473 atmospheric transport from the UK to the Arctic. *Atmospheric Environment*, 35(2): 255-267.

474 Harner, T., Farrar, N., Shoeib, M., Jones, K., Gobas, F., 2003. Characterization of polymer-coated glass
475 as a passive air sampler for persistent organic pollutants. *Environmental Science & Technology*,
476 37(11): 2 486-2 493.

477 Harvey, H. R., Taylor, K. A., Pie, H. V., Mitchelmore, C. L., 2014. Polycyclic aromatic and aliphatic
478 hydrocarbons in Chukchi Sea biota and sediments and their toxicological response in the Arctic
479 cod, *Boreogadus saida*. *Deep Sea Research Part II: Topical Studies in Oceanography*, 102: 32-
480 55.

481 Hung, H., Kallenborn, R., Breivik, K., Su, Y. S., Brorström-Lundén, E., Olafsdottir, K., Thorlacius, J. M.,
482 Leppänen, S., Bossi, R., Skov, H., Mano, S., Patton, G. W., Stern, G., Sverko, E., Fellin, P., 2010.
483 Atmospheric monitoring of organic pollutants in the Arctic under the Arctic Monitoring and
484 Assessment Programme (AMAP): 1993–2006. *Science of the Total Environment*, 408(15): 2
485 854-2 873.

486 Jaward, F., Farrar, N., Harner, T., Sweetman, A., Jones, K., 2004. Passive air sampling of PCBs, PBDEs,
487 and organochlorine pesticides across Europe. *Environmental Science & Technology*, 38(1): 34-
488 41.

489 Ke, H. W., Chen, M., Liu, M. Y., Chen, M., Duan, M. S., Huang, P., Hong, J. J., Lin, Y., Cheng, S. Y.,
490 Wang, X. R., Huang, M. X., Cai, M. G., 2017. Fate of polycyclic aromatic hydrocarbons from
491 the North Pacific to the Arctic: Field measurements and fugacity model simulation.
492 *Chemosphere*, 184: 916-923.

493 Keyte, I. J., Harrison, R. M., Lammel, G., 2014. Chemical reactivity and long-range transport potential
494 of polycyclic aromatic hydrocarbons: A review. *Chemical Society Reviews*, 45(24): 9 333-9 391.

495 Khairy, M. A., Lohmann, R., 2012. Field validation of polyethylene passive air samplers for parent and

496 alkylated PAHs in Alexandria, Egypt. *Environmental Science & Technology*, 46(7): 3 990-3 998.

497 Khairy, M. A., Lohmann, R., 2014. Field calibration of low density polyethylene passive samplers for
498 gaseous POPs. *Environmental Science -Processes & Impacts*, 16(3): 414-421.

499 Laender, F. D., Hammer, J., Hendriks, A. J., Soetaert, K., Janssen, C. R., 2011. Combining monitoring
500 data and modeling identifies PAHs as emerging contaminants in the Arctic. *Environmental
501 Science & Technology*, 45(20): 9 024-9 029.

502 Lei, P., Zhu, J. J., Pan, K., Zhang, H., 2020. Sorption kinetics of parent and substituted PAHs for low-
503 density polyethylene (LDPE): Determining their partition coefficients between LDPE and water
504 (K-LDPE) for passive sampling. *Journal of Environmental Sciences*, 87: 349-360.

505 Liss, P. S., Slater, P. G., 1974. Flux of gases across the air-sea interface. *Nature*, 247: 181-84. Doi:
506 10.1038/247181a0

507 Liu, Y., Wang, S. Y., McDonough, C. A., Khairy, M., Muir, D. C. G., Helm, P. A., Lohmann., R., 2016.
508 Gaseous and freely-dissolved PCBs in the lower Great Lakes based on passive sampling: Spatial
509 trends and air-water exchange. *Environmental Science & Technology*, 50(10): 4 932-4 939.

510 Lohmann, R., Corrigan, B. P., Howsam, M., Jones, K. C., Ockenden, W. A., 2001. Further developments
511 in the use of semipermeable membrane devices (SPMDs) as passive air samplers for persistent
512 organic pollutants: Field application in a spatial survey of PCDD/Fs and PAHs. *Environmental
513 Science & Technology*, 35(12): 2 576-2 582.

514 Lohmann, R., Dapsis, M., Morgan, E. J., Dekany, V., Luey, P. J., 2011. Determining air-water exchange,
515 spatial and temporal trends of freely dissolved PAHs in an urban estuary using passive
516 polyethylene samplers. *Environmental Science & Technology*, 45(7): 2 655-2 662.

517 Ma, J. M., Hung, H., Tian, C. G., Kallenborn, R., 2011. Revolatilization of persistent organic pollutants
518 in the Arctic induced by climate change. *Nature Climate Change*, 1(5): 255-260.

519 Ma, Y. X., Xie, Z. Y., Yang, H. Z., Möller, A., Halsall, C., Cai, M. H., Sturm, R., Ebinghaus, R., 2013.
520 Deposition of polycyclic aromatic hydrocarbons in the North Pacific and the Arctic. *Journal of
521 Geophysical Research Atmospheres*, 118(11): 5 822-5 829.

522 MacDonald, R. W., Barrie, L. A., Bidleman, T. F., Diamond, M. L., Gregor, D. J., Semkin, R. G., Strachan,
523 W. M. J., Li, Y. F., Wania, F., Alaee, M., Alexeeva, L. B., Backus, S. M., Bailey, R., Bowers, J.
524 M., Gobeil, C., Halsall, C. J., Harner, T., Hoff, J. T., Jantunen, L. M. M., Lockhart, W. L., Mackay,
525 D., Muir, D. C. G., Pudykiewicz, J., Reimer, K. J., Smith, J. N., Stern, G. A., Schroeder, W. H.,
526 Wagemann, R., Yunker, M. B., 2000. Contaminants in the Canadian Arctic: 5 years of progress
527 in understanding sources, occurrence and pathways. *Science of the Total Environment*, 254(2-
528 3): 93-234.

529 Mayer, P., Toll, J., Hermens, L., Mackay, D., 2003. Equilibrium sampling devices. *Environmental
530 Science & Technology*, 37(9): 184A-191A.

531 McDonough, C. A., Khairy, M. A., Muir, D. C. G., Lohmann, R., 2014. Significance of population centers
532 as sources of gaseous and dissolved PAHs in the Lower Great Lakes. *Environmental Science &
533 Technology*, 48(14): 7 789-7 797.

534 Meijer, S. N., Shoeib, M., Jantunen, L. M. M., Jones, K. C., Harner, T., 2003. Air-soil exchange of

535 organochlorine pesticides in agricultural soils. 1. Field measurements using a novel in situ
536 sampling device. *Environmental Science & Technology*, 37(7): 1 292- 1 299.

537 Mulder, M. D., Angelika H., Kukučka, P., Kuta, J., Příbylová, P., Prokeš, R., Lammel, G., 2015. Long-
538 range atmospheric transport of PAHs, PCBs and PBDEs to the central and eastern Mediterranean
539 and changes of PCB and PBDE congener patterns in summer 2010. *Atmospheric Environment*,
540 111: 51-59.

541 Nemr, A. E., Khaled, A., El-Sikaily, A., Said, T. O., Abd-Allah, A. M. A., 2005. Distribution and sources
542 of polycyclic aromatic hydrocarbons in surface sediments of the Suez Gulf. *Environmental*
543 *Monitoring and Assessment*, 111: 333-358.

544 Nizzetto, L., Lohmann, R., Gioia, R., Jahnke, A., Temme, C., Dachs, J., Herckes, P., Di Guardo, A., Jones
545 K. C., 2008. PAHs in air and seawater along a North-South Atlantic transect: Trends, processes
546 and possible sources. *Environmental Science & Technology*, 42(5): 1 580-1 585.

547 Nizzetto, L., Macleod, M., Borga, K., Cabrerizo, A., Dachs, J., Di Guardo, A., Ghirardello, D., Hansen,
548 K. M., Jarvis, A., Lindroth, A., Ludwig, B., Monteith, D., Perlinger, J. A., Scheringer, M.,
549 Schwendenmann, L., Semple, K. T., Wick, L. Y., Zhang, G., Jones, K. C., 2010. Past, present,
550 and future controls on levels of persistent organic pollutants in the global environment.
551 *Environmental Science & Technology*, 44(17): 6 526-6 531.

552 Ohura, T., Amagai, T., Fusaya, M., Matsushita, H., 2004. Spatial distributions and profiles of atmospheric
553 polycyclic aromatic hydrocarbons in two industrial cities in Japan. *Environmental Science &*
554 *Technology*, 38(1): 49-55.

555 Okona-Mensah, K. B., Battershill, J., Boobis, A., Fielder, R., 2005. An approach to investigating the
556 importance of high potency polycyclic aromatic hydrocarbons (PAHs) in the induction of lung
557 cancer by air pollution. *Food and Chemical Toxicology*, 43: 1 103-1 116.

558 Perera, F., Tang, D. L., Whyatt, R., Lederman, S. A., Jedrychowski, W., 2005. DNA damage from
559 polycyclic aromatic hydrocarbons measured by benzo[a]pyrene-DNA adducts in mothers and
560 newborns from Northern Manhattan, the World Trade Center Area, Poland, and China. *Cancer*
561 *Epidemiology Biomarkers & Prevention*, 14(3): 709-714.

562 Primbs, T., Simonich, S., Schmedding, D., Wilson, G., Jaffe, D., Takami, A., Kato, S., Hatakeyama, S.,
563 Kajii, Y., 2007. Atmospheric outflow of anthropogenic semivolatile organic compounds from
564 East Asia in spring 2004. *Environmental Science & Technology*, 41(10): 3 551-3 558.

565 Qi, P. Z., Qu, C. K., Albanese, S., Lima, A., Cicchella, D., Hope, D., Cerino, P., Pizzolante, A., Zheng,
566 H., Li, J. J., De Vivo, B., 2020. Investigation of polycyclic aromatic hydrocarbons in soils from
567 Caserta provincial territory, southern Italy: Spatial distribution, source apportionment, and risk
568 assessment. *Journal of Hazardous Materials*, 383: 121158.

569 Qu, C. K., Albanese, S., Lima, A., Hope, D., Pond, P., Fortelli, A., Romano, N., Cerino, P., Pizzoante, A.,
570 De Vivo, B., 2019. The occurrence of OCPs, PCBs, and PAHs in the soil, air, and bulk deposition
571 of the Naples metropolitan area, southern Italy: Implications for sources and environmental
572 processes. *Environment International*, 124: 89-97.

573 Sambrotto, R. N., Goering, J. J., McRoy, C. P., 1984. Large yearly production of phytoplankton in the

574 Western Bering Strait. *Science*, 225(4 667): 1 147-1 150.

575 Shaw, M., Mueller, J. F., 2009. Time integrative passive sampling: how well do chemcatchers integrate
576 fluctuating pollutant concentrations? *Environmental Science & Technology*, 43(5): 1 443-1 448.

577 Shen, H. Z., Huang, Y., Wang, R., Zhu, D., Li, W., Shen, G. F., Wang, B., Zhang, Y. Y., Chen, Y. C., Lu,
578 Y., Chen, H., Li, T. C., Sun, K., Li, B. G., Liu, W. X., Liu, J. F., Tao, S., 2013. Global atmospheric
579 emissions of polycyclic aromatic hydrocarbons from 1960 to 2008 and future predictions.
580 *Environmental Science & Technology*, 47(12): 6 415-6 424.

581 Staben, P. J., Van Meurs, P., 1999. Evidence of episodic on-shelf flow in the southeastern Bering Sea.
582 *Journal of Geophysical Research-Oceans*, 104(C12): 29 715-29 720.

583 Stuer-Lauridsen, F. 2005. Review of passive accumulation devices for monitoring organic
584 micropollutants in the aquatic environment. *Environmental Pollution*, 136(3): 503-524.

585 Tucca, F., Luarte, T., Nimptsch, J., Woelfl, S., Pozo, K., Casas, G., Dach, J., Barra, R., Chiang, G.,
586 Galban-Malagon, C., 2020. Sources and diffusive air-water exchange of polycyclic aromatic
587 hydrocarbons in an oligotrophic North-Patagonian lake. *Science of the Total Environment*, 738:
588 139838.

589 Venier, M., Hung, H., Tych, W., Hites, R. A., 2012. Temporal trends of persistent organic pollutants: A
590 comparison of different time series models. *Environmental Science & Technology*, 46(7): 3 928-
591 3 934.

592 Wania, F., Shunthirasingham, C., 2020. Passive air sampling for semi-volatile organic chemicals.
593 *Environmental Science-Processes & Impacts*, 22(10): 1 925-2 002.

594 Woodgate, R. A., Aagaard, K., Weingartner, T. J., 2005. A year in the physical oceanography of the
595 Chukchi Sea: Moored measurements from autumn 1990-1991. *Deep-Sea Research Part II-
596 Topical Studies In Oceanography*, 52(24-26): 3 116-3 149.

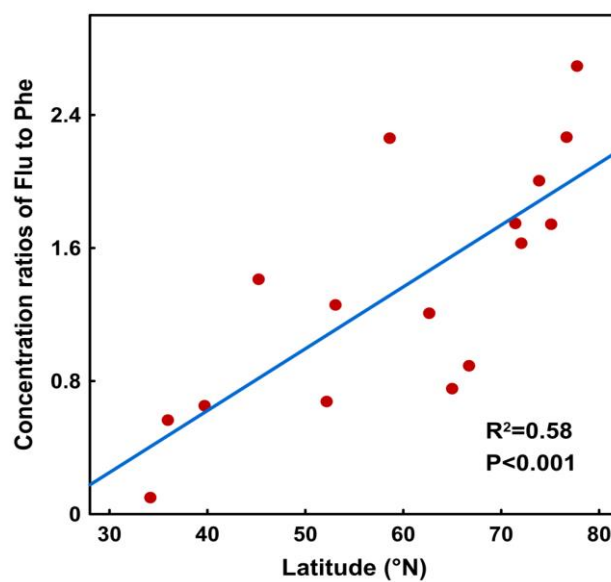
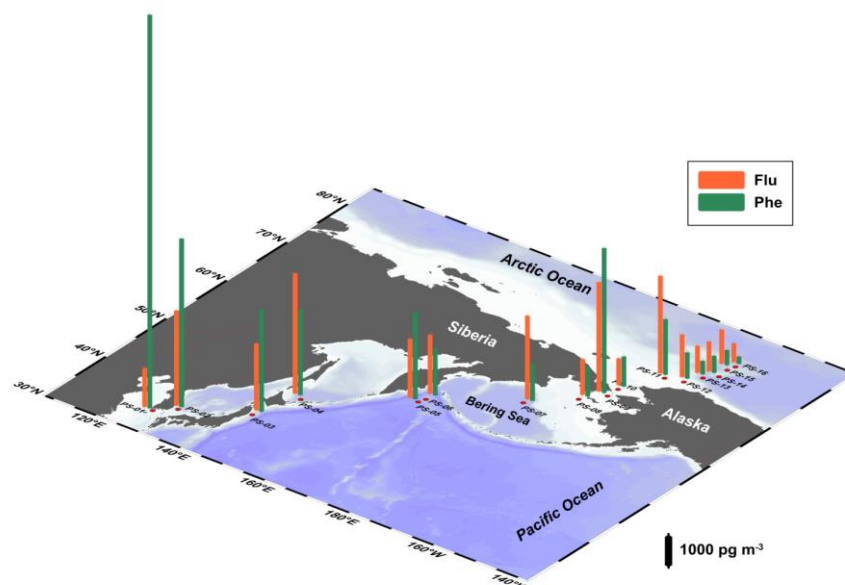
597 Wu X. W., Wang, Y., Zhang, Q. N., Zhao, H. X., Yang, Y., Zhang, Y. W., Xie, Q., Chen, J. W., 2019.
598 Seasonal variation, air-water exchange, and multivariate source apportionment of polycyclic
599 aromatic hydrocarbons in the coastal area of Dalian, China. *Environmental Pollution*, 244: 405-
600 413.

601 Yunker, M. B., Macdonald, R. W., Vingarzan, R., Mitchell, R. H., Goyette, D., Sylvestre, S., 2002. PAHs
602 in the Fraser River basin: A critical appraisal of PAH ratios as indicators of PAH source and
603 composition. *Organic Geochemistry*, 33(4): 489-515.

604 Yunker, M. B., Macdonald, R. W., Snowdon, L. R., Fowler, B. R., 2011. Alkane and PAH biomarkers as
605 tracers of terrigenous organic carbon in Arctic Ocean sediments. *Organic Geochemistry*, 42(9):
606 1 109-1 146.

607 Zhao, W. L., Cai, M. G., Adelman, D., Khairy, M., August, P., Lohmann, R., 2018. Land-use-based
608 sources and trends of dissolved PBDEs and PAHs in an urbanized watershed using passive
609 polyethylene samplers. *Environmental Pollution*, 238: 573-580.

610 Zhong, G. C., Xie, Z. Y., Cai, M. H., Moeller, A., Sturm, R., Tang, J. H., Zhang, G., He, J. F., Ebinghaus,
611 R., 2012. Distribution and air-sea exchange of current-use pesticides (CUPs) from East Asia to
612 the high Arctic Ocean. *Environmental Science & Technology*, 46(1): 259-267.



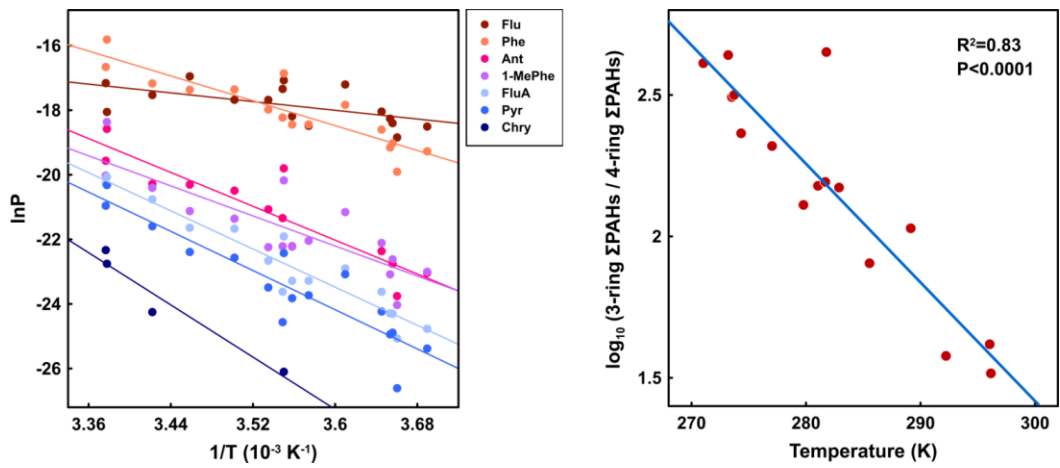
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614 **Fig. 1. The gaseous concentration distribution of Flu and Phe along the cruise transect**

615 **(the figure above), and the ratios of Flu to Phe as a function to latitude (the figure**

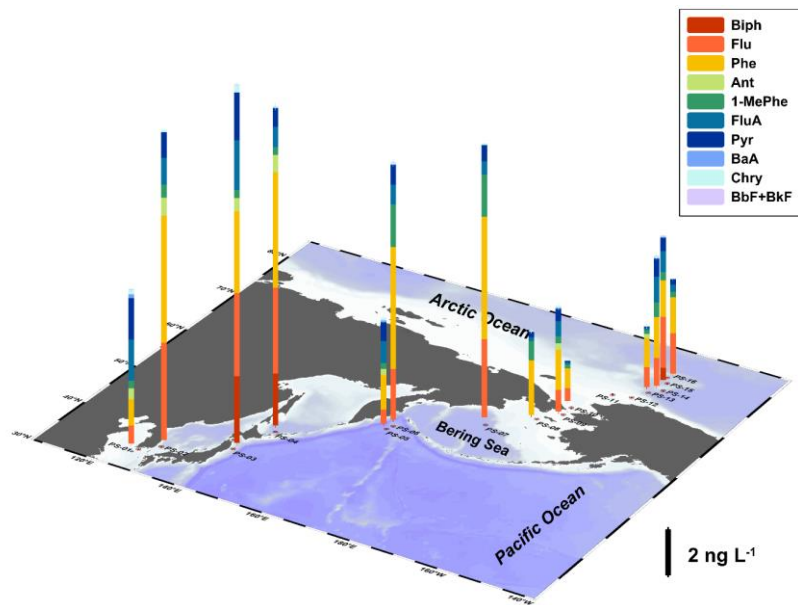
616 **below). (The domination of Flu and Phe presented in Fig. S3)**

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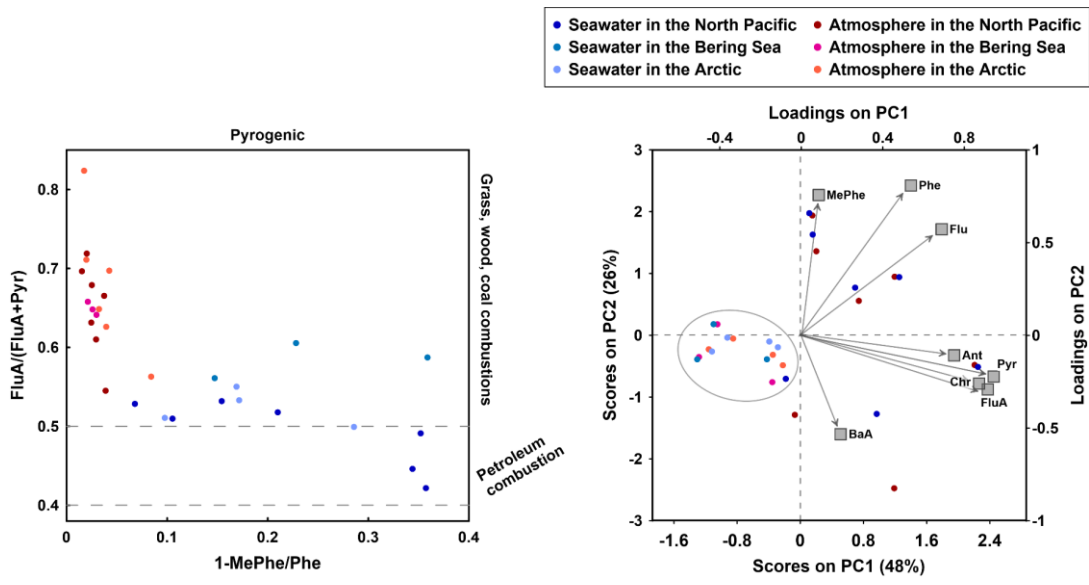
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Fig. 2. The partial pressure of PAH congeners as a function of water temperature (left), and the ratios of the sum of three-ring PAHs to four-ring PAHs as a function of air temperature (right).



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Fig. 3. The PAH concentrations in surface seawater along the cruise transect.

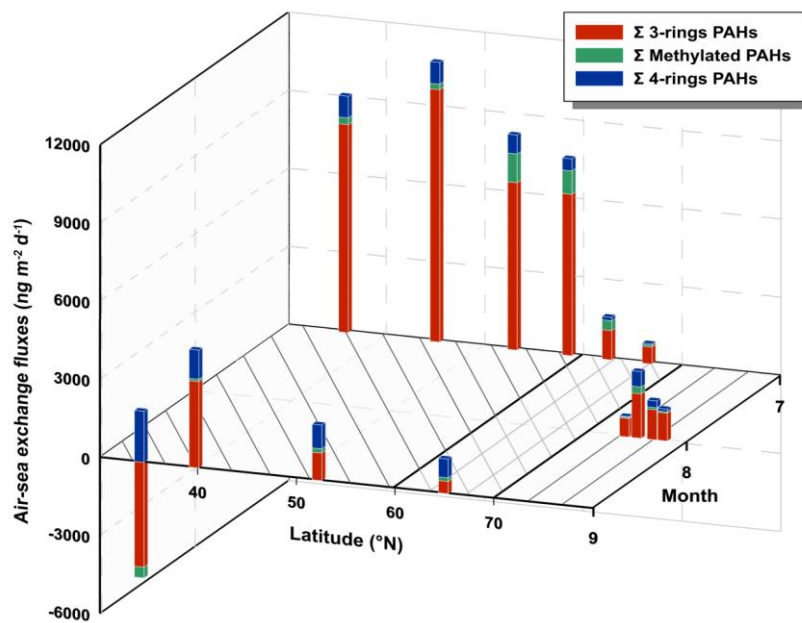
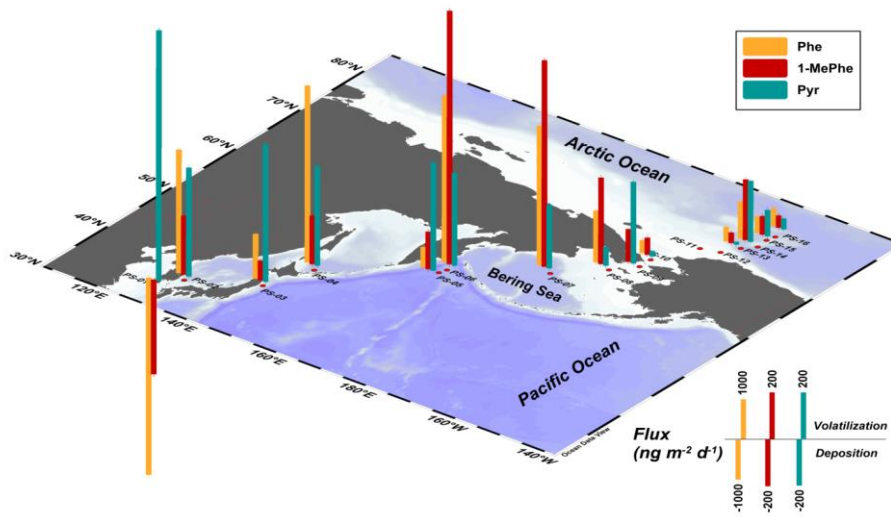


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Fig. 4. Results of PAH diagnostic ratios of MePhe/Phe and FluA/(FluA+Pyr) (left), and PCA (right) for samples in seawater (dots in blue) and atmosphere (dots in red).



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630 Fig. 5. The distribution of PAH air-sea exchange fluxes, and their monthly changes.

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