

1 Polycyclic Aromatic Hydrocarbons in ocean
2 sediments from the North Pacific to the Arctic
3 Ocean

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17 ABSTRACT

18 Eighteen polycyclic aromatic hydrocarbons (PAHs) were measured in surficial
19 sediments along a marine transect from the North Pacific into the Arctic Ocean. The
20 highest average Σ_{18} PAHs concentrations were observed along the continental slope of
21 the Canada Basin in the Arctic ($68.3 \pm 8.5 \text{ ng g}^{-1} \text{ dw}$), followed by sediments in the
22 Chukchi Sea shelf ($49.7 \pm 21.2 \text{ ng g}^{-1} \text{ dw}$) and Bering Sea ($39.5 \pm 11.3 \text{ ng g}^{-1} \text{ dw}$),
23 while the Bering Strait ($16.8 \pm 7.1 \text{ ng g}^{-1} \text{ dw}$) and Central Arctic Ocean sediments
24 ($13.1 \pm 9.6 \text{ ng g}^{-1} \text{ dw}$) had relatively lower average concentrations. The use of
25 principal components analysis with multiple linear regression (PCA/MLR) indicated
26 that on average oil related or petrogenic sources contributed ~42% of the measured
27 PAHs in the sediments and marked by higher concentrations of two
28 methylnaphthalenes over the non-alkylated parent PAH, naphthalene. Wood and coal
29 combustion contributed ~32%, and high temperature pyrogenic sources contributing
30 ~26%. Petrogenic sources, such as oil seeps, allochthonous coal and coastally eroded
31 material such as terrigenous sediments particularly affected the Chukchi Sea shelf and
32 slope of the Canada Basin, while biomass and coal combustion sources appeared to
33 have greater influence in the central Arctic Ocean, possibly due to the effects of
34 episodic summertime forest fires.

35 **Keywords:** polycyclic aromatic hydrocarbons, Arctic, sediment, source
36 apportionment.

37 **Capsule:** PAH concentrations, composition and sources is relatively heterogenous in
38 remote marine sediment from North Pacific to the central Arctic Ocean

39 INTRODUCTION

40 Polycyclic aromatic hydrocarbons (PAHs) are carcinogenic and mutagenic pollutants
41 originating from incomplete combustion and pyrolysis of carbonaceous materials
42 (Ding et al., 2007; Okona-Mensah et al., 2005). They have both anthropogenic and
43 natural sources. In particular, PAHs are well established markers with the ability to
44 trace specific sources of anthropogenic contamination (i.e. fossil fuel vs. biomass
45 combustion) and natural inputs (i.e. oil seeps, forest fires and terrestrial debris) to
46 marine systems (Jaward et al., 2004; Nizzetto et al., 2008; Yunker et al., 2002a;
47 Yunker et al., 2002b). Although PAHs represent only a small fraction (0.2–7%) of the
48 total composition of crude oil, their relative persistence in the environment and
49 potential toxicity to marine organisms warrants research into their sources and fate in
50 marine systems (Harvey et al., 2014).

51 Analysis of benthic marine sediments allows the assessment of particle settling and
52 post-depositional behavior as an important marine sink for contaminants initially
53 present in the overlying water column (Ma et al., 2015; Yunker et al., 1996). For
54 PAHs that possess relatively high organic-carbon/water partitioning coefficients (e.g.
55 $\log K_{OC} \geq 4.5$) then their sorption to organic matter (Dachs and Eisenreich, 2000) and
56 subsequent particle settling could be a significant removal process from the water
57 column. Part of the particle settling could be driven by the ‘biological pump’, which is
58 the settling flux of particle organic carbon associated with primary production by
59 phytoplankton (Dachs et al., 2002; Galban-Malagon et al., 2012). **Marine snow also**
60 **contributes significantly to the PAHs deposition in the seafloor, especially in the**

61 Arctic environment (Daly et al., 2016; Passow et al., 2012). However, the process of
62 re-mineralization during settling and diagenesis after deposition might further
63 influence the vertical removal, settling rates and residence times of PAHs in water
64 column and sediment (Adhikari et al., 2015; Adhikari et al., 2016).

65 For remote pelagic environments like the North Pacific and Arctic Oceans, then PAH
66 input is likely to be driven primarily by atmospheric deposition (MacDonald et al.,
67 2000). As PAHs have been systematically monitored in ambient Arctic air at sites in
68 Canada and the Norwegian Arctic (Becker et al., 2006; Wang et al., 2010), continental
69 sources of PAHs via long-range transport from mid-latitudes have been demonstrated
70 by several modeling studies (Halsall et al., 1997; Hung et al., 2005; Sofowote et al.,
71 2011; Wang et al., 2010). The observed air–sea gas exchange gradients of PAHs from
72 the North Pacific to the Arctic Ocean, strongly favored net deposition, with increasing
73 deposition with increasing latitude (Ma et al., 2013). However, in addition to
74 atmospheric sources and subsequent deposition to marine surfaces, the extraction and
75 processing of fossil fuels on the wide Arctic shelf seas and adjacent coastal areas
76 provides a petrogenic source of PAHs to sediments (Yunker et al., 2002a; Yunker and
77 Macdonald, 1995; Yunker et al., 2011). Climate change perturbations are also driving
78 increased coastal erosion and permafrost thawing in the Arctic (AMAP, 2012). This
79 increases the likelihood of the wider dispersal of petrogenic PAHs (McGuire et al.,
80 2009), such as transport over long distances via turbidity currents, as well as the
81 offshore transport of sediment-laden ice from the coastal shelf areas and subsequent
82 export between the shelves and the central Arctic Ocean (Belicka and Harvey, 2009).

83 The aim of this study was to examine the spatial distribution of PAHs in benthic
84 sediments from the North Pacific to the central Arctic Ocean (via the Bering Strait) to
85 infer the relevance of different PAH sources by examining their composition using
86 PAH ratios and statistical pattern recognition techniques. The study of the sedimentary
87 PAH profile can be related to sources and/or processing of these chemicals to and
88 within the marine system and this approach should be able to put long-range transport
89 and atmospheric sources into context with other petrogenic/sedimentary sources.

90

91 MATERIALS and METHODS

92 *Sampling*

93 During the 4th Chinese National Arctic Research Expedition held between July and
94 September 2010 (CHINARE 4), 0-2cm surficial marine sediment samples were
95 collected onboard the ice-breaker R/V *Xuelong* ('Snow Dragon'). The sampling cruise
96 generally covered a northward transect from the Bering Sea, through the Bering Strait
97 to the Chukchi Sea, and across the Canada Basin and central Arctic Ocean (53-88°N).
98 Detailed information about the sampling work and the sediment samples are described
99 in Supplementary Materials and listed in Table S1.

100 *Extraction, Analysis, QC/QA*

101 Extraction, fractionation and analysis of the samples was based on our previously
102 published method (Zhong et al., 2012), and is described in more detail in the
103 Supplementary Materials. Eighteen PAH compounds were analysed in this research,
104 including 16 parent-PAHs and 2 alkylated-PAHs: naphthalene (Nap),

105 1-methylnaphthalene (1-MN), 2-methylnaphthalene (2-MN), acenaphthylene (Acl),
106 acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant),
107 fluoranthene (Fluor), pyrene (Py), benzo[a]anthracene (BaA), chrysene (Chry),
108 benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP),
109 indeno[1,2,3-cd]pyrene (InP), dibenz[a,h]anthracene (DBahA), benzo[ghi]perylene
110 (BghiP). A PAH-Mix containing 9 deuterated compounds (see Table S2) were added
111 as surrogate standards to monitor matrix effects with ^{13}C -PCB 208 added as an
112 injection standard. The recoveries of target PAHs ranged from $60 \pm 3\%$ to $91 \pm 7\%$ in
113 5 spiked samples. In total five procedural blanks were extracted together with the
114 samples. The method detection limits (MDLs) for each PAH were derived from the
115 procedural blanks and quantified as the mean field blank plus three times the standard
116 deviation (3σ) of the field blanks. MDLs ranged from 0.001 ng/g for BkF to 0.053
117 ng/g for Nap. The major PAH contamination found in the procedural blanks
118 comprised of Nap, Phe and Py with concentrations of 0.028 ± 0.008 , 0.019 ± 0.007
119 and 0.017 ± 0.007 ng/g, which account for $< 1.1\%$ of those compounds in the
120 sediment samples.

121

122 RESULTS and DISCUSSION

123 *Geographic Distribution of PAHs*

124 The total concentrations of 18 PAHs in the surface sediment ($\Sigma_{18}\text{PAHs}$, sum of the
125 detected 16 parent PAHs and 2 alkyl-PAHs) ranged from 8.5 to 78.3 ng g⁻¹ dry weight
126 (dw), with a mean of 37.3 ± 24.0 ng g⁻¹ dw over the entire cruise track. The sampling

127 stations were separated into five geographical areas as: Bering Sea, Bering Strait,
128 Chukchi Sea, Canadian Basin margin and Central Arctic Ocean to assess the spatial
129 distribution of the PAHs. A summary of the chemical concentrations in these areas is
130 presented in Table 1 and the spatial distribution of Σ_{18} PAHs along the cruise track is
131 shown in Figure 1. Analysis of variance (ANOVA) demonstrated significant
132 differences in the mean concentrations between the five geographical regions.

133 The highest average Σ_{18} PAHs concentrations were observed in the Canada Basin
134 margin region ($68.3 \pm 8.5 \text{ ng g}^{-1} \text{ dw}$), followed by sample stations in the Chukchi Sea
135 ($49.7 \pm 21.2 \text{ ng g}^{-1} \text{ dw}$) and Bering Sea ($39.5 \pm 11.3 \text{ ng g}^{-1} \text{ dw}$), while the Bering
136 Strait ($16.8 \pm 7.1 \text{ ng g}^{-1} \text{ dw}$) and Central Arctic Ocean ($13.1 \pm 9.6 \text{ ng g}^{-1} \text{ dw}$) had
137 relatively lower average concentrations. It is noteworthy that concentrations of
138 Σ_{18} PAHs showed a wide variability in the Chukchi Sea with high levels observed in
139 sediments at sites SR11 ($78.3 \text{ ng g}^{-1} \text{ dw}$) and C07 ($75.8 \text{ ng g}^{-1} \text{ dw}$) in the northern
140 Chukchi Sea shelf, as well as site BN03 in the Chukchi Sea marine bench edge (71.8
141 $\text{ ng g}^{-1} \text{ dw}$). Relatively lower concentrations were observed at sites SR01 (8.8 ng g^{-1}
142 dw) and SR04 ($27.7 \text{ ng g}^{-1} \text{ dw}$) in the southern Chukchi Sea shelf and site M02 (28.6
143 $\text{ ng g}^{-1} \text{ dw}$) in the Chukchi Sea basin. However, in the margin edges of the Canada
144 Basin, high Σ_{18} PAHs levels were observed at sites S26 ($75.5 \text{ ng g}^{-1} \text{ dw}$) and MS02
145 ($70.5 \text{ ng g}^{-1} \text{ dw}$), respectively. Compared with legacy POPs in surficial sediment of
146 the same region, some differences exist for their spatial distribution patterns. OCs and
147 PCBs all had significantly higher concentrations in the relatively shallow water of the
148 Bering-Chukchi shelf areas compared to the deeper water regions of the Bering Sea

149 and Arctic Ocean. Lower PAHs levels in the surface sediment of Bering Strait might
150 be due to particle mediated biodegradation processes. But for continental shelf
151 margins of the Chukchi Sea and Canada Basin, some additional petrogenic sources
152 other than atmospheric sources might also contribute to the PAHs observed in benthic
153 sediments and this is discussed in detail below.

154 Compared with the distribution of PAHs in the atmosphere and surface seawater in the
155 same regions (which were also observed in the same cruise (see Ma et al., 2013)), the
156 PAH occurrence in the sediment was quite different. Generally, the atmospheric PAHs
157 over the Arctic Ocean displayed higher concentrations than those observed over the
158 North Pacific Ocean and this was attributed to ‘within Arctic’ sources at the time of
159 the cruise (Arctic summer), while a decreasing trend in concentrations in surface
160 seawater was observed with increasing latitude. This was possibly due to more
161 effective biogeochemical removal processes in the water column (Ma et al., 2013).
162 Although the observed air–sea gas exchange gradients strongly favored net deposition
163 of PAHs, their efficient removal from surface waters and the water column via particle
164 mediated biodegradation may reduce efficient transfer of these chemicals to deep
165 water environments and benthic sediments (Berrojalbiz et al., 2011; Lohmann et al.,
166 2009; Yunker et al., 2002a). The remineralization of particulate organic carbon along
167 the vertical transport gradients results in the release and recycling of sorbed PAHs,
168 and cycling of PAHs in the sediments (Adhikari et al., 2015). Sediment mixing can
169 result to such distinct distribution of PAHs between seawater and sediments (Adhikari
170 et al., 2016; Tarr et al., 2016). In addition to atmospheric sources, petrogenic sources

171 such as oil seeps and export of PAH-laden sediments from coastal regions to the shelf
172 margins might also contribute to the PAHs observed in benthic sediments, particularly
173 in the continental shelf margins of the Chukchi Sea and Canada Basin and this is
174 discussed further below.

175 Compare with PAHs in other Arctic surrounding sea regions, the present results for
176 the Chukchi Sea and edge of Canada Basin sediments are comparable to PAHs
177 observed in Kara Sea (not detected -110 ng g⁻¹) and Svalbard coast (25-38 ng g⁻¹), but
178 lower than those in Barents Sea (18-500 ng g⁻¹) and Beaufort Sea Shelf (290-1200 ng
179 g⁻¹) (Jiao et al., 2009; Sericano et al., 2001; Yunker et al., 1996). For sediments
180 obtained from the central Arctic Ocean, our results are also comparable to
181 concentrations obtained in the Makarov Basin, but about 10-fold lower than those
182 observed in the Amundsen and Nansen Basins (Yunker et al., 2011). While in
183 comparison with other ocean area, our results are significantly lower than PAHs
184 observed in North Sea (700-2700 ng g⁻¹) and Baltic Sea (9.53-1870 ng g⁻¹) (Klamer
185 and Fomsgaard, 1993; Witt, 1995).

186 The TOC level in these surficial sediments (see Table S1) was higher in the shelf
187 regions of the Bering Strait (average value of 0.64%) and Chukchi Sea (average value
188 of 0.60%), and decreased towards the Bering Sea (average value of 0.43%), Canada
189 Basin margins (average value of 0.27%), and the central Arctic Ocean (average value
190 of 0.10%). Moreover, correlations were not so strong between Σ_{18} PAHs and TOC for
191 the entire cruise ($r^2=0.367$, $p<0.05$, $n=30$). No significant correlations have been
192 observed between PAHs and TOC in other Arctic regions reported before (Yunker et

193 al., 2011). For persistent organic pollutants (POPs), such as PCBs, weak or
194 insignificant relationships were obtained between TOC and these chemicals (Ma et al.,
195 2015). Since the sedimentation rates varied across the study transect, the surficial
196 sediment samples collected here (collected to a depth of ~2 cm) represent sediment
197 that has accumulated over greatly differing time periods. Sedimentation rates along
198 the edge of the continental shelf of the Chukchi Sea with the Canada Basin (i.e., the
199 Chukchi-Alaskan margin) ranged from 0.4 to 12 m/kyr with average rates of between
200 1.50 and 3.13 m/kyr, while the sedimentation rates were estimated only to be
201 0.01–0.02 m/kyr in the central Arctic Ocean. Thus for the higher sedimentation rate
202 regions such as the northern Bering and Chukchi Seas, the sediments comprise of
203 material that has accumulated over the last few decades. While for the material
204 collected in the lower accumulation regions (e.g. Canada Basin and central Arctic
205 Ocean) the sediments represent accumulation over 100s of years and hence represent
206 time periods when PAH sources and input to the deep ocean environment may have
207 changed considerably (Darby et al., 2009). Additionally, although some PAHs may
208 reach the deep water environment associated with organic matter, water-column and
209 sediment layer processing such as biodegradation and re-partitioning of PAHs to
210 mineral matter, may account for the weak relationship observed between TOC and
211 chemicals like PAHs present in remote marine oceans.

212

213 *PAH Composition*

214 Generally, the lighter PAHs such as Nap, its alkylated derivatives (1-MN and 2-MN),

215 and Phe, with average concentrations ranging 4–6 ng g⁻¹ dw, were the most abundant
216 PAHs in the sediments along the cruise track, and contributed >50% to Σ_{18} PAHs. The
217 higher MW PAHs such as Chry, BbF and BghiP, had lower concentrations of 2–3 ng
218 g⁻¹ dw. Levels of other detected PAHs were lower, with average concentrations \leq 1 ng
219 g⁻¹ dw. Moreover, although only two alkyl-PAHs were measured in this study (1-MN
220 and 2-MN), they were more abundant than their parent PAH (Nap) at all locations
221 along the cruise (Figure 2). Previous studies indicate that the alkyl-substituted PAHs
222 in sediment are likely derived from petrogenic inputs and this dominance of
223 alkyl-PAHs has been previously reported in sediments collected from the northeastern
224 Chukchi and Beaufort Sea shelves (Harvey et al., 2014; Yunker et al., 1996). **Although**
225 **it varies with sampling location, Adhikari et al., 2015, 2016 have reported that the**
226 **alkylated PAHs contribute to the major vertical fluxes and also contribute**
227 **significantly to the PAHs distribution in the northern Gulf of Mexico sediments even**
228 **in natural background conditions (Adhikari et al., 2015; Adhikari et al., 2016).**

229 The PAH profile observed in surface seawater and boundary-layer air over the same
230 oceanic transect was dominated by the lower MW PAHs, with 2-MN, Phe and Py
231 contributing about 50% to the dissolved Σ_{18} [PAHs]_{wat} in the seawater. However,
232 concentrations of atmospheric heavier 5-6 ringed PAHs, which were mainly detected
233 in the particulate phase, were quite low, while their levels were extremely low in
234 surface seawater (Ma et al., 2013). Therefore, similarities in the PAH profile between
235 the atmosphere, surface seawater and benthic sediments are apparent for the low MW
236 PAHs only, although it is difficult to ascertain the influence of atmospheric sources on

237 the PAHs present in benthic sediments, especially given water column ‘processing’
238 prior to and during particle settling (Harvey et al., 2014).

239

240 *Source Identification by MDR*

241 Two different molecular diagnostic ratios (MDR) were calculated to estimate the
242 influence of potential sources for the PAHs present in the sediment. The ratios of
243 Fluor/(Fluor + Py) and InP/(BghiP + InP) in the surface sediment along the cruise
244 tracks ranged from 0.26 to 0.57 and from 0.14 to 0.61, respectively, suggesting a
245 well-mixed source profile of petrogenic, petrogenic-combustion, as well as biomass
246 and coal combustion origin (Figure 3-a). Similarly, a well-mixed source profile was
247 also demonstrated for surface seawater from the North Pacific to the Arctic Ocean by
248 MDR, however, MDR applied to the boundary-layer air of the same region indicated
249 combustion of biomass or coal only as the principle sources of PAHs (Ma et al., 2013).

250 MDRs however should be interpreted with some caution due to different
251 environmental processing of the isomers during atmospheric transport and water
252 column vertical transport such as biodegradation, photo-oxidation (Galarneau, 2008).

253 MDRs calculated here provide a relative assessment between the various marine
254 compartments. They demonstrate that part of the PAH component in the sediments,
255 surface seawater and atmosphere share the same source profile, which to some extent
256 might be due to air-sea gas exchange and subsequent transfer through the water
257 column, although differences in the MDR indicate a degree of ‘uncoupling’ between
258 these compartments..

259 Specifically, in the sediments of Bering Sea, the ratios of Fluor/(Fluor + Py) and
260 InP/(BghiP + InP) were <0.4 and 0.2 respectively, indicating a petrogenic source
261 (Figure 3-b). While for the Chukchi Sea shelf and slope of the Canadian Basin region,
262 Fluor/(Fluor + Py) and InP/(BghiP + InP) were higher and ranged from 0.39-0.48 and
263 0.19-0.34 respectively, indicating mixing sources of petrogenic-derived and petroleum
264 combustion-derived PAHs (Figure 3-c). The dominance of the two alkyl PAHs (1-MN
265 and 2-MN) also support the petrogenic influence on the PAHs observed in these
266 sediments (Figure 2). The Chukchi Sea, for example, is estimated to contain 15 billion
267 barrels of recoverable oil, with potential for this region to serve as a significant source
268 of oil and natural gas in the future given that drilling rights have now been permitted
269 (Harvey et al., 2014). PAH petrogenic markers might originate in oil from naturally
270 occurring seeps on the Chukchi shelf, although this petrogenic signal might be
271 localized and not extend to sediments in the continental shelf regions of the Canada
272 Basin or central Arctic Ocean (Gautier et al., 2009). In addition, coastal
273 terrestrially-derived PAHs might contribute to the sedimentary PAH profile in the
274 Chukchi Sea shelf region and margins of the continental shelf. The organic-rich peat,
275 shales, bitumens and coals that cover Alaska's North Slope tundra provide likely
276 sources of alkyl-PAHs, with transport of particle matter over long distances via
277 turbidity currents or ice rafting of sediments (Jones and Yu, 2010). Similarly, the
278 Mackenzie River might supply elevated concentrations of alkyl-PAHs through the
279 delivery of eroded bitumen from the watershed to the Canadian shelf (Yunker et al.,
280 2002b; Yunker et al., 1996), a process that could be exacerbated by climate change in

281 the Arctic (McGuire et al., 2009).

282 For several sample sites in the central Arctic Ocean, it is noteworthy that observed
283 ratios of Fluor/(Fluor + Py) and InP/(BghiP + InP) indicate biomass combustion
284 sources (Figure 3-d). Moreover, the contribution of parent PAH relative to alkyl-PAHs
285 (ratio of Nap/(1-MN + 2-MN)) increased significantly in the central Arctic Ocean
286 (Figure 2). To some extent, this suggests increasing import of parent PAHs on
287 sedimentary PAHs in the central Arctic Ocean. Combustion PAH emissions from
288 forest and prairie fires are dominated by parent PAHs which are transported
289 atmospherically, as well as by the movement of sea and river ice with ice-associated
290 particulate matter (Gelinas et al., 2001; Schmidt and Noack, 2000; Yunker et al.,
291 2002b). During the CHINARE 2010 cruise, a clear increase of atmospheric PAHs,
292 especially particle-bound PAHs, was observed in the central Arctic Ocean region, and
293 attributed to forest fires in sub-Arctic regions of Alaska, Canada, Russia and Siberia
294 during summer (Ma et al., 2013). From our results, these episodic inputs of pyrogenic
295 PAHs appear to contribute to the PAHs present in the deep ocean sediments of the
296 central Arctic Ocean, although significant PAH ‘weathering’ is likely to occur
297 between the marine/atmosphere interface and the deep ocean sediments. **The use of
298 PAH ratios as source markers is limited once environmental weathering processes
299 (chemical and biological) preferentially degrade/remove one PAH relative to another
300 (Galarneau, 2008).**

301

302 *Source Apportionment Pattern Recognition and Multiple Linear Regression*

303 In order to have a quantitative understanding of the contributions of different PAH
304 sources, principal component analysis (PCA) followed by multiple linear regression
305 (MLR) of the data was used as the source apportionment method. Specifically, PCA
306 allowed us to represent the total variability of the original PAH data in a minimum
307 number of factors and the following MLR is used to determine the percent
308 contribution of different PAH sources to the sediments of the entire cruise. The
309 detailed procedure of PCA/MLR analysis was followed as previously reported by
310 Larsen and Baker (2003) and is described in more detail in the Supplementary
311 Materials. For the PCA results, three significant factors were determined which
312 explained 88% of the total variability of the original PAH dataset (Table 2). The first
313 factor was responsible for 32% of the total variance with a profile of Fluor, Py, Flu,
314 BaP and BaA, which indicated wood and coal combustion. It is reported that some of
315 the lower MW PAHs like Fluor, Py and Flu are predominantly indicative of low to
316 medium temperature combustion (i.e. inefficient combustion processes) associated
317 with biomass combustion such as wood, but also coal combustion (Harrison et al.,
318 1996; Simcik et al., 1999). The second factor was responsible for 29% of the total
319 variance. This factor was predominately composed of Nap, 1-MN, 2-MN, Ace and
320 Phe. These low MW PAHs in addition to the presence of alkyl-PAHs indicate that this
321 factor was mainly dependent on oil related sources (Larsen and Baker, 2003; Yunker
322 et al., 1996). The third factor accounted for 27% of the total variance and was
323 predominately weighted by the higher MW PAHs such as IP, DBahA, BghiP BbF and
324 BkF. These 5-6 ringed PAHs are mainly attributed to high temperature pyrogenic

325 sources such as liquid fossil fuel combustion (Larsen and Baker, 2003; Venkataraman
326 et al., 1994). Moreover, results of the following MLR showed that the mean percent
327 contribution is 42.3% for the oil related sources, 32.1% for the wood and coal
328 combustion sources, and 24% for the high temperature pyrogenic sources. It is
329 noteworthy that the oil-related sources contributed to nearly half of the PAHs in the
330 surficial sediments collected along the cruise transect, demonstrating that
331 natural/petrogenic sources were important for the PAHs present in these remote ocean
332 sediments, and indicating a degree of ‘uncoupling’ between the broad
333 combustion-derived PAHs in the atmosphere and those present in benthic sediments.

334

335 *Conclusions*

336 This study provides insight into the PAH concentrations and composition in remote
337 marine sediments in a transect that is relatively heterogenous with regards to the
338 varied depth that the sediments were collected from i.e. shallow continental-shelf seas
339 vs. deep ocean environments, and the rate of sedimentation. The evidence supporting
340 the role played by petrogenic sources is based on examining only 18 PAHs and a
341 more extensive set of analytes including alkanes, tricyclic terpanes, steranes and
342 hopanes as biomarkers would be useful alongside a wider set of alkylated-PAHs to
343 help distinguish specific source categories such as weathered oil, coal and eroded
344 terrigenous material. Nonetheless, in comparison to our earlier study that examined
345 the same PAHs in air and surface seawater along broadly the same transect (Ma et al.,
346 2013), there are notable differences in the PAH profile between these ‘surface’

347 compartments and the sediments measured here. Notably the ratios of Fluo/Pyr and
348 InP/BghiP are markedly lower in the sediments of the Chukchi Sea shelf and
349 continental slope of the Canada Basin compared to air and surface water, supporting
350 the petrogenic nature of the PAHs in these sediments. Furthermore, our findings show
351 that the PAHs in the sediments of the central Arctic Ocean are dominated by
352 non-fossil fuel combustion sources and is supported by the study of Yunker et al.
353 (2011) who noted that the ubiquitous occurrence of allochthonous coal in surficial
354 sediments made source attribution from other petrogenic sources (and probably other
355 sources as well) difficult to determine. We recommend that for future campaigns –
356 driven by the need to understand contemporary pollution sources to air and surface
357 waters - then a much broader set of geochemical organic analytes be screened for in
358 collected sediment samples, and that chemical profiles be benchmarked against the
359 chemical profiles observed in sediments that are dominated by petrogenic sources.

360

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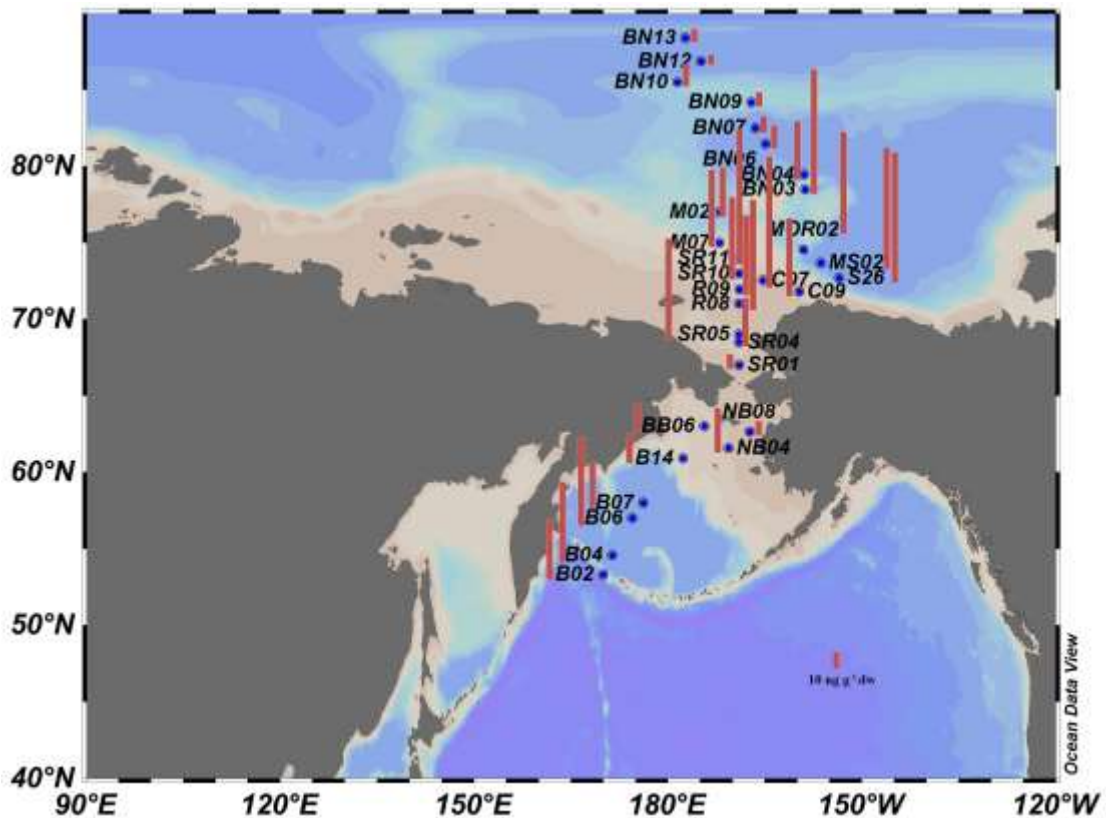
511 **Figure Captions**

512 **Figure 1.** Concentrations of PAHs (Σ_{18} [PAHs]) in the surface marine sediment along
513 **the sampling cruise.**

514 **Figure 2.** Contributions of Nap, 1-MN & 2-MN, other 2-3 ring PAH and 4-6 ring PAH
515 to the Σ PAH in the five geographical regions.

516 **Figure 3.** Ratios of InP/(BghiP+InP) vs. Fluor/(Fluor+Py) in surface sediment along
517 the cruise (a), in Bering Sea (b), Chukchi Sea shelf and slope of the
518 Canadian Basin (c) and in the central Arctic Ocean (d).

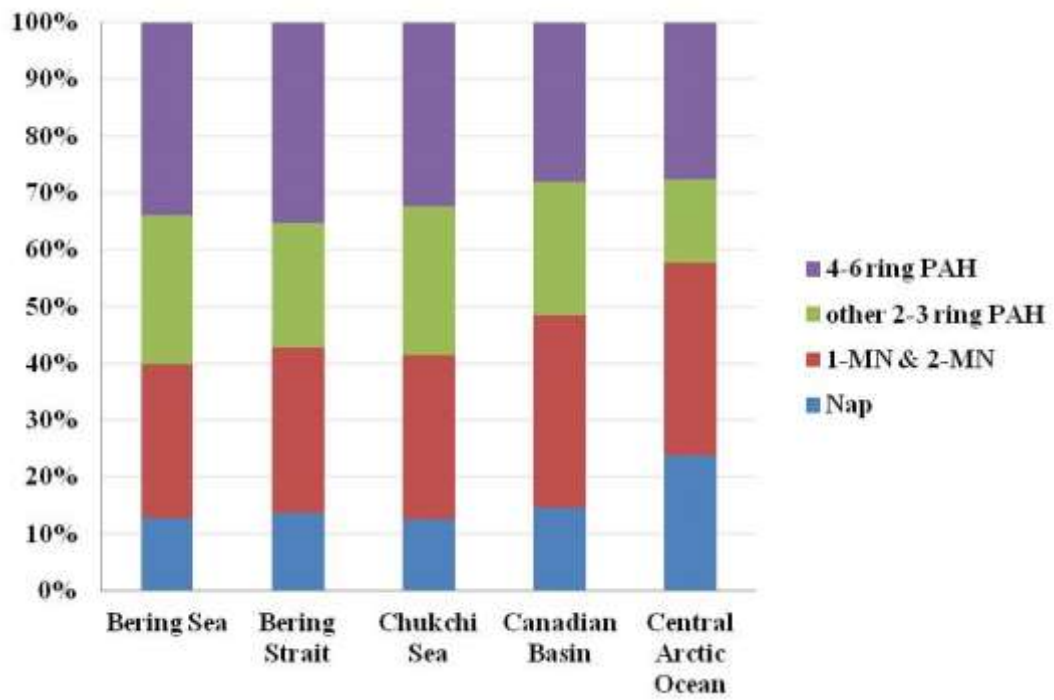
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521 **Figure 1.**

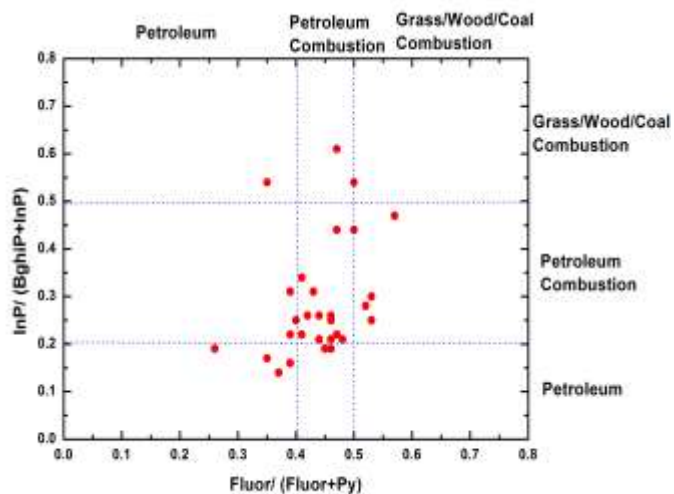
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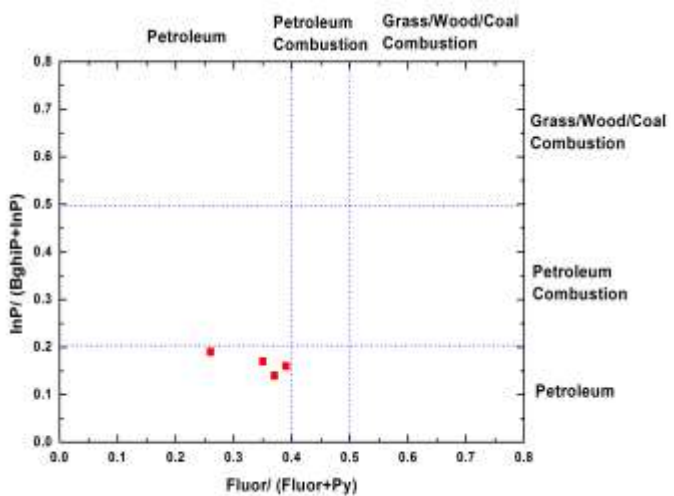
524 **Figure 2.**

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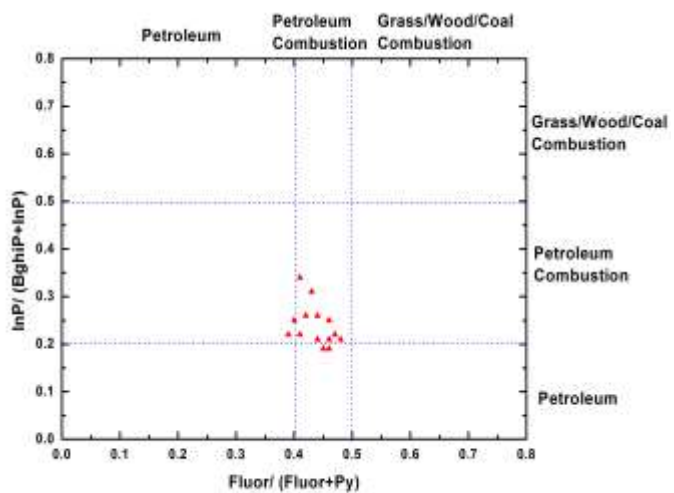
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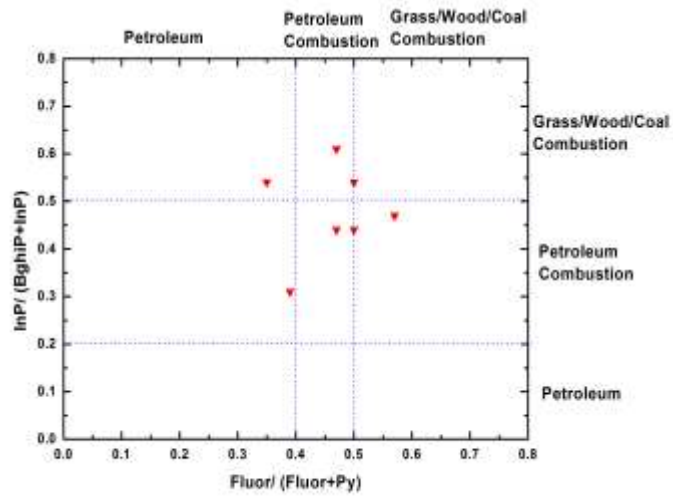
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530 **Figure 3.**

531 **Table 1.** Summary of Σ_{18} PAHs concentrations (ng g^{-1} d.w.) in the surface sediment of
 532 the Bering Sea, Bering Strait, Chukchi Sea, Canadian Basin and Central Arctic Ocean
 533 for CHINARE 4 expedition.

	Range	Median	Mean	S.D.
Bering Sea	26.2-51.2	40.4	39.5	11.3
Bering Strait	8.5-25.8	16.5	16.8	7.1
Chukchi Sea	8.8-78.3	47.0	49.7	21.2
Canadian Basin	58.9-75.5	70.5	68.3	8.5
Central Arctic Ocean	5.8-33.9	9.7	13.1	9.6
Entire Cruise	5.8-78.3	34.2	37.3	24.0

534

535
 536 **Table 2.** PAH variance explained and loadings of three significant factors by source
 537 apportionment PCA analysis.

	Factor 1 32%	Factor 2 29%	Factor 3 27%
Fluor	.823	.429	.291
Py	.807	.397	.359
Flu	.805	.495	.042
BaP	.784	.163	.502
BaA	.703	.251	.270
Chry	.665	.544	.477
Acl	.654	.650	.357
Ant	.430	.145	-.136
Nap	.195	.943	.152
twoMN	.330	.912	.204
oneMN	.408	.873	.237
Ace	.631	.728	.200
Phe	.581	.695	.297
IP	.121	.081	.951
DBahA	.373	.231	.889
BghiP	.405	.181	.867
BbF	.402	.354	.820
BkF	-.216	.168	.736

538