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

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ABSTRACT

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

Keywords: polycyclic aromatic hydrocarbons, Arctic, sediment, source apportionment.

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

INTRODUCTION

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

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

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

MATERIALS and METHODS

91

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 (Σ_{18}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 ± 8.5 ng g^{-1} dw), followed by sample stations in the Chukchi Sea

135   (49.7 ± 21.2 ng g^{-1} dw) and Bering Sea (39.5 ± 11.3 ng g^{-1} dw), while the Bering

136   Strait (16.8 ± 7.1 ng g^{-1} dw) and Central Arctic Ocean (13.1 ± 9.6 ng g^{-1} 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 ng g^{-1} dw) and C07 (75.8 ng g^{-1} dw) in the northern

140   Chukchi Sea shelf, as well as site BN03 in the Chukchi Sea marine bench edge (71.8

141   ng g^{-1} dw). Relatively lower concentrations were observed at sites SR01 (8.8 ng g^{-1}

142   dw) and SR04 (27.7 ng g^{-1} dw) in the southern Chukchi Sea shelf and site M02 (28.6

143   ng g^{-1} 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 ng g^{-1} dw) and MS02

145   (70.5 ng g^{-1} 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

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

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

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

PAH Composition

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

10

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 ≤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*

In order to have a quantitative understanding of the contributions of different PAH

sources, principal component analysis (PCA) followed by multiple linear regression

(MLR) of the data was used as the source apportionment method. Specifically, PCA

allowed us to represent the total variability of the original PAH data in a minimum

number of factors and the following MLR is used to determine the percent

contribution of different PAH sources to the sediments of the entire cruise. The

detailed procedure of PCA/MLR analysis was followed as previously reported by

Larsen and Baker (2003) and is described in more detail in the Supplementary

Materials. For the PCA results, three significant factors were determined which

explained 88% of the total variability of the original PAH dataset (Table 2). The first

factor was responsible for 32% of the total variance with a profile of Fluor, Py, Flu,

BaP and BaA, which indicated wood and coal combustion. It is reported that some of

the lower MW PAHs like Fluor, Py and Flu are predominantly indicative of low to

medium temperature combustion (i.e. inefficient combustion processes) associated

with biomass combustion such as wood, but also coal combustion (Harrison et al.,

1996; Simcik et al., 1999). The second factor was responsible for 29% of the total

variance. This factor was predominately composed of Nap, 1-MN, 2-MN, Ace and

Phe. These low MW PAHs in addition to the presence of alkyl-PAHs indicate that this

factor was mainly dependent on oil related sources (Larsen and Baker, 2003; Yunker

et al., 1996). The third factor accounted for 27% of the total variance and was

predominately weighted by the higher MW PAHs such as IP, DBahA, BghiP BbF and

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'

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

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374

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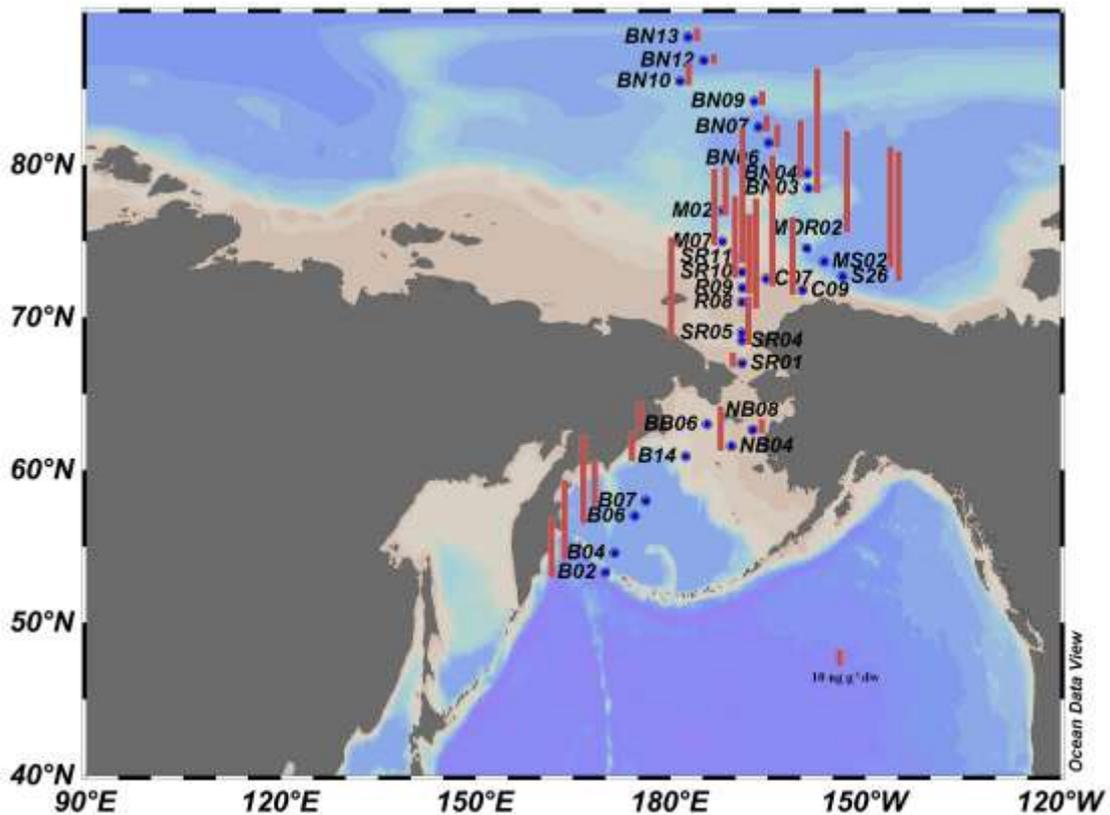508   Ocean. Environmental Science & Technology 46, 259-267.
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Figure Captions

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

the sampling cruise.

Figure 2. Contributions of Nap, 1-MN & 2-MN, other 2-3 ring PAH and 4-6 ring PAH

to the ΣPAH in the five geographical regions.

Figure 3. Ratios of InP/(BghiP+InP) vs. Fluor/(Fluor+Py) in surface sediment along

the cruise (a), in Bering Sea (b), Chukchi Sea shelf and slope of the
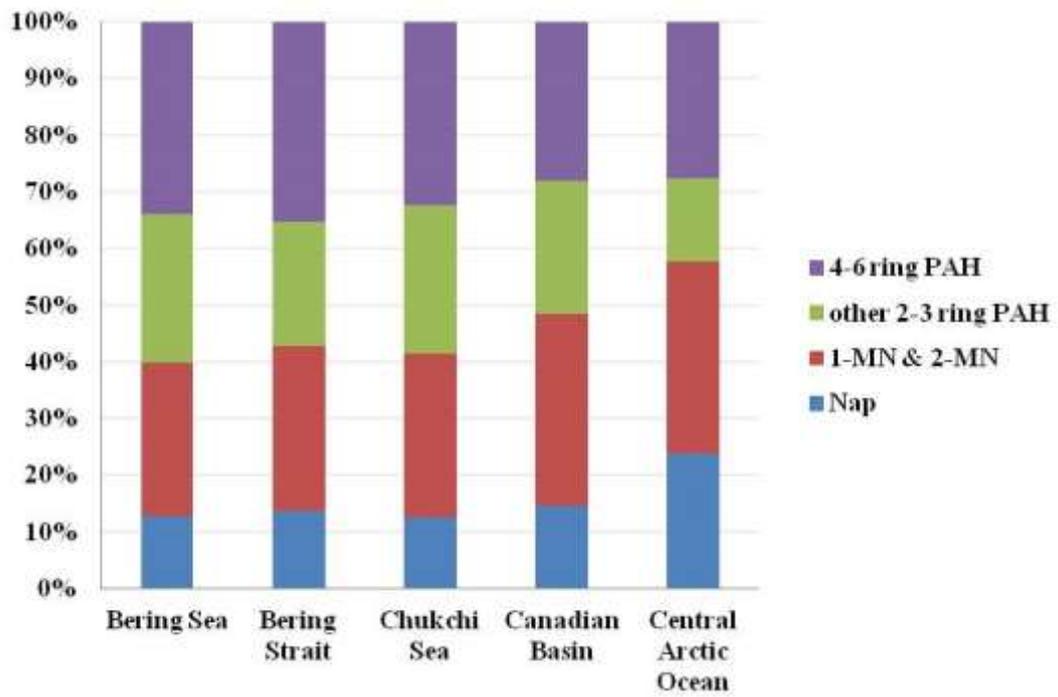
Canadian Basin (c) and in the central Arctic Ocean (d).

Figure 1.

523

Figure 2.
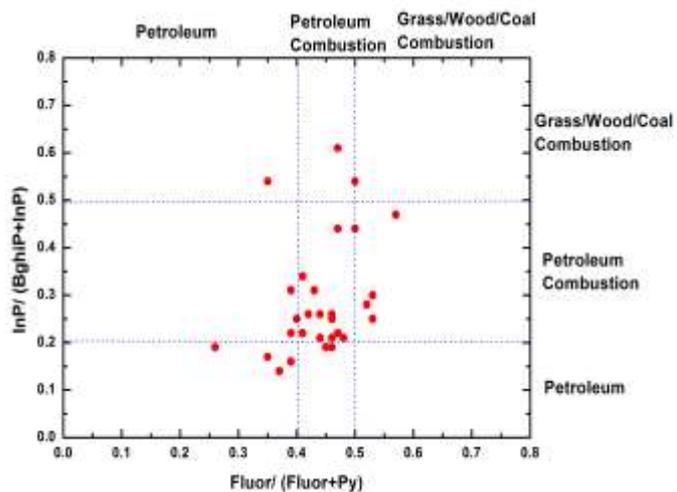
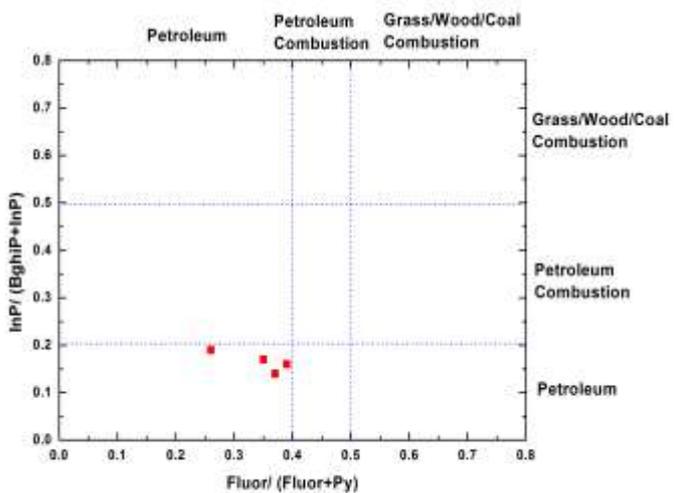525

526   **a**

527   **b**

528   **c**

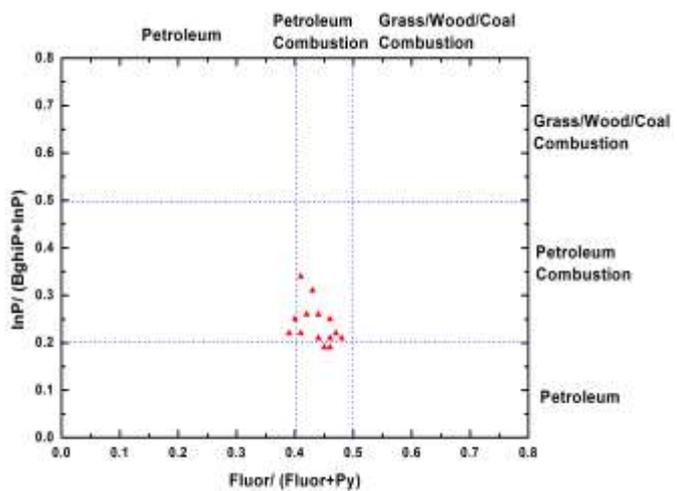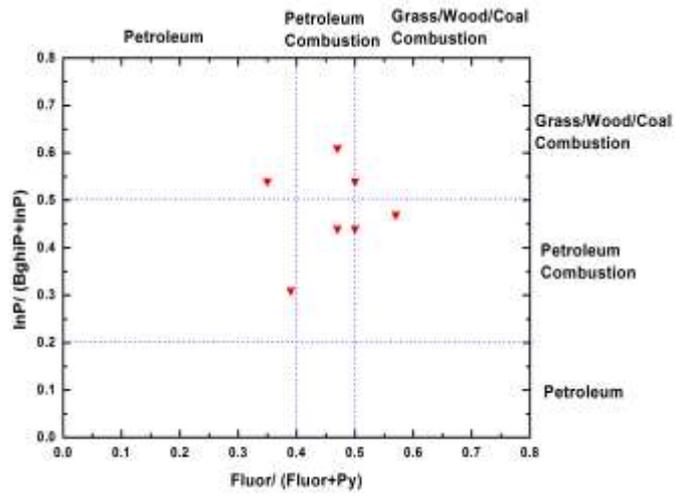529   **d**

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.

Donations	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